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DEVELOPMENT AND OPTIMIZATION OF POWDERS FOR LARGE AREA POWDER COATINGS

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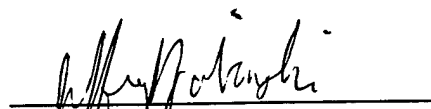DTIC QUALITY INSPECTED 1   20000525 028

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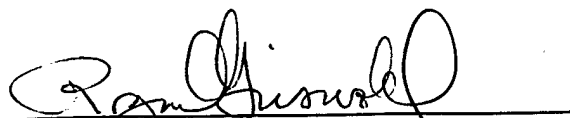
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13. ABSTRACT *(Maximum 200 words)*
Technologies with the potential to produce mono-disperse powders for HVTS application and pigmented polymer beads for advanced aircraft coatings formulations were evaluated under this program. Conventional spray atomization techniques, including supercritial fluid spray atomization, and REES processing were determined to be ineffectual in meeting the objectives. However, experimental results of supercritial GAS processing and inkjet production methods demonstrated the potential of each of these technologies to produce the desired products. Additional formulation development and process optimization work will have to be performed before sufficient quantities (10 lbs) of materials can be produced for HVTS testing and evaluation.

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EXECUTIVE SUMMARY

The Materials Laboratory (WL/MLBT) at Wright-Patterson Air Force Base is conducting research to develop advanced aircraft coating technologies for improved cleanability, durability, and service life. Two of the most promising technologies currently under investigation include: (1) the use high velocity thermal spray (HVTS) techniques to apply organic coatings; and (2) advanced, low VOC (volatile organic compound) coatings that incorporate pigmented polymer beads.

The technical requirements for organic powder coatings applied by HVTS include specific size and distribution, density, shape, and resistance to electrostatic clumping. The preferred size range for HVTS is 20 to 60 μm and approximately 10 μm for pigmented polymer beads. Tight particle size distributions are critical in HVTS application for proper mass transfer and uniform transfer of kinetic energy on impact. Pigmented polymer beads incorporated in coating formulations offer significant advantages with regard to improved flow, reduced viscosity, improved durability, and cleanability. Hiding and tinting properties may also be improved, particularly with vesiculated morphologies. Improved flow characteristics and reduced viscosity is imparted by the regular geometry of the pigmented polymer beads. Conventional powder production methods are not suited for producing materials for these applications. As such, a need exists to develop methods to produce materials for the Air Force to further research efforts and to eventually support the transition of this technology to a production environment.

During the course of the program, METSS investigated a number of promising technologies for the production of uniform powders of controlled size and shape including:

- inkjet technologies

- spray atomization techniques

- supercritical fluid processing techniques, including:
    - $\Rightarrow$ supercritical fluid (SCF) spray atomization techniques
    - $\Rightarrow$ rapid expansion of supercritical solutions (RESS)
    - $\Rightarrow$ supercritical gas anti-solvent (GAS) processing techniques.

The most promising technologies identified for achieving the program objectives were inkjet printing technologies and supercritical gas anti-solvent (GAS) processing technique. The technical feasibility of using inkjet processing methods (including state-of-the-art acoustic printing methods) to manufacture HVTS powders and pigmented polymer beads was clearly demonstrated under program, including the production of solid and hollow core spheres. GAS processing experiments also demonstrated favorable results, particularly with regard to the use GAS processing to create pigmented polymer beads which may be used in the formulation of durable, cleanable coatings for improved service life. However, the capability of using GAS processing techniques to create mono-disperse polymer beads of the size range needed for HVTS coatings (20 to 60 μm) may be limited. The particle production methods demonstrated by METSS are well suited for process commercialization.

The project, as it was entered into, was very ambitious as it was the overall objective of this program not only to identify technologies to produce mono-disperse polymer powders, but to provide sufficient quantities of materials for further testing and evaluation by the Air Force. This not only included materials for application by the HVTS process, but also pigmented.

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TABLE OF CONTENTS

LIST OF FIGURES

Due to the large amount of photo-quality images used in the production of this report, all report figures are presented in an appendix to this report (Appendix B).

1.0 INTRODUCTION AND BACKGROUND

1.1 Background

The Materials Laboratory at Wright-Patterson Air Force Base is conducting research to develop advanced aircraft coating technologies for improved cleanability, durability, and service life. Two of the most promising technologies currently under investigation include: (1) the use high velocity thermal spray (HVTS) techniques; and (2) advanced, low VOC (volatile organic compound) coatings that incorporate pigmented polymer beads.

High velocity thermal spray is a new technique for applying organic coatings based on thermal spray or plasma spray technologies conventionally used for inorganic coatings. The main advantage of HVTS is that it eliminates the need for subsequent drying/curing operations. Fully developed, HVTS will bring powder coating technology to the field and facilitate the use of powdered coating technology on large parts (i.e., parts too big for oven curing). In the HVTS process, a dry powdered coating is directed at the surface being coated at a velocity high enough to ensure melting and coalescence of the powder particles upon impact with the surface. Relatively good results have been achieved using conventional powder coatings, however, the distribution in particle size of conventional powder coatings is thought to be too broad for proper film formation via the HVTS process. This translates into a distribution in the kinetic energy of the particles impacting the surface being coated and leads to the deposition of a non-uniform film. Furthermore, the fines in the conventional powder coatings (particles less than 10 μm in diameter) disrupt the plasma by creating eddy currents and turbulence, thus further disrupting the deposition process. It is desirable to create a source of powdered coatings for HVTS application with a very narrow distribution in properties, including particle size, shape, and density to circumvent these problems.

While the use of pigmented polymer beads is not a new concept in industrial coatings, it is a concept that is currently being revisited in light of the current mission statement of the Air Force with regard to advanced aircraft coatings and the demanding issues of environmental compliance. Pigmented polymer beads incorporated in coating formulations offer advantages with regard to improved flow, reduced viscosity, improved durability, and cleanability. Hiding and tinting properties may also be improved, particularly with vesiculated morphologies. Improved flow characteristics and reduced viscosity is imparted by the regular geometry of the pigmented polymer beads. This, in turn, facilitates a reduction in the VOC content of the coating formulation as the amount of solvent used in the coating formulation may be decreased in relative proportion to the reduction in viscosity. Durability and cleanability are imparted by the physical nature of the particles themselves, which impart mechanical stability to the coating film and create a harder, abrasion resistant surface. The surface properties of the coating can be further improved if the bulk density of the pigmented beads is controlled to facilitate migration of the beads to the surface of the coating during application and curing. The bulk density of the polymer beads can be controlled through proper selection of the polymers used in the production of the pigmented polymer beads or by controlling the morphology of the pigmented polymer beads, e.g., the production of pigmented polymer beads with vesiculated morphologies.

1.2   Technical Requirements

The technical requirements for organic powder coatings applied by HVTS include specific size and distribution, density, shape, and resistance to electrostatic clumping. The preferred size range for HVTS is 20 to 60 μm and approximately 10 μm for pigmented polymer beads. Tight particle size distributions are critical in HVTS application for proper mass transfer and uniform transfer of kinetic energy on impact. Conventional methods of producing powder coatings are not suited to produce materials of this specific nature. As such, a need exists to develop methods to produce thermal spray powder materials to further research efforts and to eventually support the transition of this technology to a production environment.

Larger and smaller size particles may be produced using various techniques but the ranges of production fall outside current needs for thermal spray powder systems. Examples include:

- Emulsion polymerization can produce particles up to about 5 μm in size. Above this level the emulsion stabilization techniques are ineffective and coagulation and agglomeration occur.

- Micro-suspension polymerization has not been extended to particle sizes much greater than 20 μm and is additionally limited by the types of chemistries that can be practiced.

- Grinding and classifying methods used in conventional powder coating production produce non-uniform particle shapes with a larger distribution than required and a significant population of smaller particles and fines that are not suited for thermal spray technologies.

1.3   Candidate Technologies

During the course of the program, METSS investigated a number of promising technologies for the production of uniform powders of controlled size and shape including:

- inkjet technologies
- spray atomization techniques
- supercritical fluid processing techniques, including:
  ⇒ supercritical fluid (SCF) spray atomization techniques
  ⇒ rapid expansion of supercritical solutions (RESS)
  ⇒ supercritical gas anti-solvent (GAS) processing techniques.

The primary reasons for considering each of these candidate technologies are reviewed briefly in this section.

1.3.1   Adaptation of Inkjet Technologies

The unique properties of inkjet printing technologies lend themselves to the production of uniform resin droplets. These droplets may be dried to produce organic powder coatings for thermal spray application having a tight distribution in the desired range. Both thermoplastic

and thermoset powder coating systems can be processed using inkjet technology provided solution or melt viscosity can be reduced sufficiently for droplet formation. Direct particle formation in the correct size range with a narrow particle size distribution may be a benefit of using this technology provided the properties of the inkjet unit can be precisely controlled and local non-uniformity's in the polymer solution can be avoided. Hardware for the proof of concept efforts can be adapted from standard off-the-shelf inkjet printing equipment.

The current piezoelectric materials used to drive the inkjet printers may operate continuously at approximately 300 °F, but can be operated up to 500 °F for shorter time periods. Heating elements would be required in either case. While this is a non-standard option, it may be necessary to facilitate the use of inkjet technologies for higher molecular weight solutions and low viscosity polymer melts. Alternatively, reactive liquid monomers may be cured via directed energy immediately after particle formation and ejection from the print head. Activation methods suitable for this type of system and free radical chemistry include UV cure, thermal (convection or IR), and microwave technologies. Other activation methods for use with urethane and epoxy chemistry may also be possible, for example the use of an amine processing atmosphere to drive the chemical cure reaction. By controlling the activation energies and the chemistries employed, particles having different levels of residual activity may be prepared.

The application of inkjet printing technology to the production of HVTS powders is possible due to advances in the field of high resolution inkjet printing. Basic inkjet printing involves supplying a polymeric based ink to a printing head which contains a piezoelectric transducer to facilitate droplet formation. Supporting electronics and electrostatic controls then accelerate and guide the ink particle to the target print surface in the desired pattern. Rapid developments in the hardware area for the production of higher resolution imaging has occurred since 1988, improving the dot per inch (dpi) capability of printers from 167 to 600 dpi. The 600 dpi technology will make it possible for METSS to produce 40 to 60 micron particles. Working fluid viscosity and surface tension are two of the primary factors that METSS will need to consider to produce different particle sizes using a single inkjet print head.

1.3.2 Spray Atomization Techniques

Conventional spray atomization technologies were investigated to determine the ability of these techniques to produce uniform powder particles for thermal spray applications. Previous works have demonstrated the size and population of droplets that can be produced by conventional spray technologies are of the order of interest for the particles needed for thermal spray technologies. Conventional spray coating technologies use air to atomize coatings into droplets and propel them to the surface being coated. Atomization is a process that is fairly simple to accomplish for most liquids since all that is needed is a high relative velocity between the liquid to be atomized and the surrounding air. The velocity differential creates hydrodynamic and aerodynamic forces that cause the liquid to disintegrate into drops. As might be expected, the atomization process is very sensitive to paint rheology and the methods used to atomize the coating. Conventional air spray applicators facilitate atomization by impinging a high velocity air stream on a relatively low velocity paint stream. Airless and air-assisted spray technologies create the same effect by forcing the paint through a small orifice (nozzle) at high pressures. Atomization occurs rapidly as the paint ligaments disintegrate into drops. The process is generally complete within a few centimeters of the spray nozzle. Conventional applicators may operate at low pressures or high pressures, high flow rates or

low flow rates. The resultant spray pattern (droplet size, distribution, and shape) depends on nozzle design, operating conditions (both environmental and equipment), and the rheological properties of the liquid system (paint).

Conventionally, once the paint spray particles are created, they are propelled to the surface being coated, where they impinge, flow, coalesce and dry. In order to manufacture resin particles for subsequent thermal spray application, the particles should be solidified at a given point in flight and collected. Various means may be used to accomplish this. For example, a conventional "shot tower" approach may be used to allow the particles to air dry to a specific size, conventional spray drier technologies may also be used, or artificial heating may be applied to slow dry (convection) or flash dry the particles in flight using infrared heating or microwave technologies. Since the droplets do not have to flow and coalesce to form a coating on a substrate, the fraction of medium and slow drying solvents that facilitate these actions may modified to control droplet formation. Thus, the resin systems used to produce the thermal spray powders may be based on existing but modified coating systems.

1.3.3 Supercritical Fluid Processing Techniques

Supercritical fluid (SCF) technologies may be used to produce 20 to 60 micron size particles for thermal spray application, or particles less than 10 μm in diameter for pigmented polymer beads. Specifically, there are three approaches based on SCF technology that merit investigation for the production of thermal spray powders and pigmented polymer beads:

1. the application of SCF paint spray technologies to produce atomized droplets

2. the application of RESS (rapid expansion from supercritical solutions) technologies

3. the application of GAS (gas anti-solvent) technologies.

1.3.3.1 SCF Spray Atomization

The first process is simply an extension of the conventional spray atomization approach previously discussed - the obvious exception being the use of supercritical paint spray technology (i.e., the UNICARB® process) to produce the atomized droplets. The production of solid droplets using conventional paint spray technologies may be limited by an inability to remove solvent from the paint droplets in an efficient manner, causing the particles to coalesce or clump. In the SCF paint spray process, supercritical carbon dioxide is used as the diluent solvent for the paint formulation so it flashes off almost instantaneously once the paint spray exits the nozzle. The medium and fast drying solvents may be removed from the SCF paint formulation to facilitate particle formation.

1.3.3.2 RESS Processing

Rapid expansion from supercritical solutions (RESS) has demonstrated the production of polymeric micro-particles and micro-spheres in the 5 to 90 micron range, thus offering another novel approach for the production of thermal spray powders and pigmented polymer beads. Supercritical fluids have a high degree of solvent power across a broad range of solubility. The solvent characteristics of these fluids can be readily modified by changes in pressure and temperature in the range above the critical point of the supercritical fluid, or by the addition of a solvent modifier. Carbon dioxide is a common supercritical fluid used to dissolve a number of

organic systems. In the RESS process, a supercritical fluid solution is expanded across an orifice resulting in rapid development of a uniform, highly supersaturated solution. The sudden expansion of these solutions through a nozzle results in a sudden loss of solvent power and precipitation of the solutes of uniform particle size. Since the solvent is typically a gas at ambient conditions it is completely separated from the particles during the process, thus eliminating the need for further drying and creating a one step process for particle formation.

The use of RESS techniques has not only demonstrated a capacity to produce single component particles with uniform particle size distributions, but these same techniques have been used to produce dual phase particles of a core/shell configuration through the simultaneous co-precipitation of two solutes from one solvent system. The core/shell geometry is obtained through a difference in solubility limit between the two dissolved solutes. Upon precipitation, the core is formed by the fast precipitating solute. The slower precipitating solute then coats the core particle to form the shell. Thus, RESS technologies may be used to create two-component reactive thermal spray systems of a core-shell geometry. Researchers at Ohio State University have recently used this technique to produce Naproxen particles coated with poly L-lactic acid.

1.3.3.3 GAS Processing

Gas anti-solvent (GAS) technologies may also provide a suitable means of producing organic powders for thermal spray application and the production of pigmented polymer beads for advanced coating applications. In the GAS process, a liquid solution containing the compound to be precipitated is sprayed into a chamber containing the supercritical (gaseous) anti-solvent. The supercritical fluid expands the liquid solution and lowers its density, dilating the liquid particle and dissolving the liquid carrier, thus causing the solute to nucleate uniformly into fine particles. The expanded solvent phase consisting primarily of SCF is then filtered to remove the entrained particles and then separated via a drop in pressure to yield a gas (anti-solvent component) and a liquid (organic solvent) suitable for recycle. The GAS process can be used in conjunction with any atomization technique to remove trapped solvents and nucleate particle formation. The GAS process may provide an alternative means of "drying" paint droplets created using conventional paint spray technologies.

2.0 OBJECTIVE AND APPROACH

2.1 Task Order Objective

The objective of this program is to optimize powder manufacturing techniques for High Velocity Thermal Sprayed (HVTS) coatings. These powders will be utilized in a program designed for the deposition of low volatile organic content (VOC) coatings by conventional and HVTS techniques.

2.2 Approach

A program plan was developed at the onset of the program and presented to the Air Force for review and comment. Due to the exploratory nature of this program, the approach was straightforward: review the literature for technical insights and direction and perform key laboratory experiments to evaluate candidate technologies and test production concepts. Thus, the overall program approach could be summarized in two broad tasks:

- **Task 1. Literature Search** - A literature search was performed to investigate candidate technologies for producing powders used in high performance HVTS applications. The literature search identified pertinent technical information needed for a valid technical evaluation of the production methods under assessment. Key production variables were identified, as well as any technical or commercial limitations. Emphasis was placed on the candidate technologies discussed previously. Task 1 sub-tasks were defined as:

  ⇒ Literature Search
  ⇒ Literature Review
  ⇒ Technical Evaluation
  ⇒ WL/MLBT Briefing

- **Task 2. Process Evaluation** - The ability of each of the candidate techniques to produce thermoplastic and thermoset powder coatings for HVTS application or pigmented polymer beads was determined. The production of vesiculated and unvesiculated morphologies was considered, with the production of core-shell geometry's for two-component systems and pigmented polymer beads emphasized. Key experiments and demonstrations to test the potential production concepts were identified along with reformulation efforts that may be required to produce the high performance coatings by the various methods of investigation. Process modifications or post-processing steps required to produce powders in the size ranges required (20 to 60 μm for HVTS powders and of the order of 10 μm for pigmented polymer beads) were identified. Task 2 sub-tasks were defined as:

  ⇒ Process Considerations
  ⇒ Equipment Modifications
  ⇒ Initial Testing
  ⇒ Solid Powders
  ⇒ Pigmented Polymer Beads
  ⇒ Core-Shell Geometry's.

3.0 DESCRIPTION OF EFFORTS

In this section, a description of the actual program efforts is presented. Emphasis is placed on the technologies best suited for meeting the objectives of the program. However, a technical evaluation is provided for each of the technologies investigated with their advantages and disadvantages clearly presented.

3.1 Literature Search, Review, and Initial Technical Evaluation

A literature search and review was performed at the onset of the program along with an initial technical evaluation of the information gathered. The initial technical evaluation determined which technologies would be pursued the most vigorously, thus defining the overall direction of the experimental program.

METSS performed an extensive computerize literature search on various topics related to the program objectives at the onset of the program. All of the papers of potential interest were retrieved and reviewed. An outline of the key work search is provided in Table 3.1 cross-referenced by major topic. Emphasis was placed on the literature that emphasized particle processing techniques. The results of the literature search were favorable, as a number of works were identified that directly supported the objectives of the program and provided valuable insights that were used to direct the program efforts. The literature search was complemented by phone interviews with industrial contacts and various experts in academia who were contacted to comment on their work in the various areas of interest to the program.

An initial technical evaluation of the potential powder production processes was performed based on the results of the literature search and personal discussions with industry and academia. The results of the initial technical evaluation are presented in Section 4.1. The results of the literature search and the initial technical evaluation were presented to the staff of WL/MLBT at a technical briefing held at Wright-Patterson AFB, Ohio on August 8, 1996.

3.2 Process Evaluation

The process evaluation efforts were quite extensive, running continually through the course of the program. The process evaluation efforts consisted of a number of iterative laboratory experiments for each of the processes under consideration. Additional technical efforts were pursued to support the process evaluation efforts as needed. A summary of the technical efforts performed during the course of the program is presented in this section.

3.2.1 Materials Identification, Acquisition, and Qualification

Pre-formulated powder coatings were used as the base materials to support the process development efforts. This made it possible to avoid formulation development efforts during the proof of concept experiments while still ensuring that the materials used were representative of commercially viable coating formulations with reasonable physical properties. This approach was especially beneficial with regard to the two-component crosslinking systems of interest to the Air Force. At least one powder coating sample was ordered for each of the resin classes of interest to the Air Force.

Table 3.1. Literature Search Criteria

Major Topic	Key Words
Inkjet or Inkjet	• polymer • particle • thermal
Rapid Prototyping	• development • technique or method • inkjet or ink jet
Supercritical	• antisolvent • rapid expansion • spray • atomization • precipitation • RESS • GAS • PCA
Powder	• manufacture or production • size • distribution • coating
Spray or Atomization	• coating • polymer
Spray Drying	• polymer • coating
Pigments	• polymer • bead • paint or coating • encapsulate
polymer	• particle and production • microballoon

A number of supporting experiments were performed on the materials received to assist in the subsequent processing experiments, including:

- using differential scanning calorimetry (DSC) to determine processing temperature ranges of the materials acquired to support the program objectives

- identifying suitable solvents for the powder coating materials and the saturation limits of the polymers in solvent solutions

- investigating the effect of solvent type, concentration, and temperature on solution and melt viscosity's.

DSC experiments were performed on all of the coating materials tested. Solvent effects and viscosity measurements were primarily limited to the thermoset materials where good solvents were easily identified that could potentially be used in commercial processing operations. METSS determined the solubility limit of the thermoset coating resins (epoxies and polyurethanes) in MEK and acetone and then determined the viscosity of the polymer solutions as a function of concentration and temperature. The resultant data were used to select the appropriate solutions for the subsequent processing experiments. In the GAS process, low solution viscosity's are required to allow the polymer solution to be pumped through an orifice into the gas anti-solvent chamber (supercritical CO_2). In the inkjet process the solvent is necessary to reduce the viscosity of the polymer to a point where it can be pumped through the inkjet nozzle and broken up into droplets by the mechanical perturbations introduced by the piezoelectric device driving the inkjet head. A solution viscosity of less than 100 cPs is desired for inkjet processing. Pertinent results are presented in Section 4.2.1.

3.2.2 Spray Drying

The particles produced by the inkjet process and spray atomization techniques required some mechanism to solidify the droplets produced. Spray drying techniques were thought to be the most viable option, therefore METSS constructed an experimental system to support the initial laboratory experiments. Development efforts were performed using PVC piping and galvanized ducting to determine the most efficient system design. The fluids that were actually processed in the technology evaluation experiments were used to support design optimization.

3.2.3 Spray Atomization

The potential of using spray atomization techniques to produce mono-disperse powders was reviewed under the program, with an emphasis on the application of SCF spray atomization techniques. Experiments performed in support of this evaluation essentially involved melting polymer resins in a reactor, mixing the polymer melt with supercritical CO_2, and then pumping the solution through a nozzle (a modified UNICARB® approach). In this process, the supercritical CO_2 acts as a diluent solvent to reduce the viscosity of the polymer solution so it can be pumped through the nozzle.

The ability of supercritical fluid spray atomization techniques to generate mono-disperse HVTS powders was investigated through two experimental procedures. Initial experiments were performed using an ISCO SFX 2-10 supercritical fluid extractor. The instrument's plumbing was modified to support the flow of the high viscosity polymer melt through the capillary extraction tubes. Initial experiments were static with regard to polymer melt-CO_2 mixing. Later experiments involved the use of a 1 liter high pressure, stirred reactor that made it possible to induce melt mixing of the supercritical CO_2 with thermoplastic polymer melts or thermoset polymer solutions. CO_2 pressure was used to atomize the melt/solution as it was expelled from the pressurized chambers. Temperature and pressure could be controlled on both units. Variables of interest in the spray atomization experiments included temperature, pressure, the residence time required to get good CO_2 mixing, the addition of co-solvents and solvent levels, and the size (L/D ratio) and temperature of the outlet nozzle.

3.2.4 RESS Experiments

The primary objective of the laboratory RESS experiments was to identify the appropriate supercritical fluids and processing conditions required to dissolve the polymer systems of interest (this effort was supported by the literature), and then identify the conditions required to precipitate the polymer from the supercritical solution. Upstream and downstream temperatures, pressure drop, and the L/D ratio (length/diameter) of the nozzle were the key experimental variables. A schematic of the equipment used to conduct the RESS experiments performed under the is presented in Figure 3.1. RESS experiments were primarily limited to low molecular weight polyethylene resins, using several different supercritical fluids, including carbon dioxide, propane, and ethane.

3.2.5 GAS Experiments

A large number of GAS experiments were performed under the program. The objective of these experiments was to identify the exact processing techniques needed to create mono-disperse powder product via the GAS process. All of the GAS experiments were performed using epoxy solutions. Various solvents were tested, including acetone, MEK, and methylene chloride. Polymer concentration was varied widely. Pigmented and un-pigmented solutions were tested. GAS processing conditions investigated included:

- pressure and flow rate of the polymer solution into the GAS expansion chamber
- total amount of polymer solution introduced during the experiment
- pressure and temperature of the GAS chamber
- static and dynamic CO_2 flow conditions
- con-current and counter-current CO_2 flow (relative to the point of solvent introduction)
- the use of surfactants to modify particle nucleation and growth behavior
- nozzle diameter and shape
- powder collection methods
- post processing extraction time.

Solvent expansion experiments (with supercritical CO_2) were performed to assist in the selection of suitable GAS processing conditions. The powders produced by the GAS process were analyzed under the microscope and via SEM. Image analysis techniques were used to measure particle size and distribution data. The SEM data were used to direct further processing efforts.

Initial GAS experiments and the solvent expansion experiments were performed using a Jerguson gage (approximately 300 ml in volume) to facilitate process viewing and expansion measurements. However, the majority of the GAS experiments were performed in a large 2.75 liter pressure vessel to facilitate processing of larger quantities of solution. Schematics of the GAS process are provided in Figures 3.2 for co-current (a) and counter-current (b) flow arrangements. ISCO 2000 pumps were used to pressurize the GAS chamber, maintain CO_2 pressure and flow conditions, and to introduce the solvent solutions into the GAS chamber.

These pumps allowed control over flow rate or pressure, but not both. Ideally, independent control over both variables is preferred.

A typical GAS process experiment is performed as follows:

The process begins by pressurizing the SFE vessel. This is performed by opening all valves between the CO_2 tank and the vessel via the CO_2 pump. The tank will stabilize to the tank pressure within approximately fifteen minutes. The SFE vessel is brought to the operating pressure by filling the CO_2 pump, pressurizing to a given pressure, and pumping to the vessel. This procedure is very repetitive and time-consuming, and can take over an hour to pressurize a vessel of this size. The solution should be prepped prior to the experiment. The pigment may be allowed to settle if its presence is not desired. The pump used to introduce the solution into the GAS chamber should be cleaned prior to use by flushing the pump with a full volume of the main solvent in the solution. The pump should then be charged with the solution and brought to operating pressure prior to the onset of the experiment.

During the GAS experiment, the solution is pumped into the vessel for a set period of time at a constant pressure or constant flow rate. Post processing extraction steps may be used after all of the solution is processed if additional extraction time is required to extract all of the solvent from the powder or remove excess solvent from the GAS chamber to prevent further interaction between the polymer and the solvent. Post processing conditions may vary from those used during the GAS precipitation procedure.

While the solution is being introduced into the chamber, constant care must be taken to ensure the flow rate of CO_2 through the chamber is maintained at a rate sufficient to allow the pressure in the chamber to remain constant. This can be achieved by adjusting the outlet valve so that the rate of gas flow out of the system matches the combined inlet rate for the CO_2 and solution.

Under typical operating conditions CO_2 inlet/outlet flows are maintained at 15 ml/min for 50 min, solution inlet rate is set at 0.5 to 5 ml/min for 5 to 25 minutes, and the pressure of the GAS chamber is maintained between 900 and 1400 psi. Heating tape can be used to maintain temperature within the chamber at this operating pressure. The internal temperature of the chamber is measured via a thermocouple.

3.2.6 Inkjet Experiments

The inkjet experiments were severely hampered under the program due to the limited availability of technical support in this mature industry and continued delays in equipment delivery. During the initial part of the program, METSS expended a great deal of effort trying to identify appropriate expertise in the field of inkjet printing to support the technical evaluation of this potential mode of processing. This turned out to be a considerable challenge as there has been very little work performed using inkjet technology to produce droplets of anything but inks. Thus, it was difficult to obtain answers to even the simplest of questions, including questions regarding the maximum fluid viscosity's that can be processed using commercially available equipment.

The only company identified with an appropriate degree of expertise and experience in processing materials other than inks was Codent (UK). Codent has performed several tasks processing waxes and monomers (acrylic monomers flashed cured after droplet formation) at viscosity's up to 100 cPs (most inks are of the order of 3 cPs). Thus, discussions with Codent provided METSS with the direction needed to drive formulation efforts (i.e., create solutions with viscosity's less than 100 cPs) and a source for the equipment needed to support the inkjet experiments.

After mutually defining the program needs, Codent proposed to develop and provide METSS with an experimental inkjet system to support the developmental program. The system Codent proposed was a completely integrated inkjet dispensing system, requiring only that METSS supply the stream of fluid to be processed and control over the fluid pressure. Since it was unknown whether a continuous inkjet device or a drop on demand system would be appropriate for the present task, the electronic drivers for the system were constructed to support either type of print head. Most importantly, the system was designed with the ability to vary pulse shape, amplitude, and frequency across a broad bandwidth to allow the processing conditions for the polymer solutions to be optimized. A strobe feature with a variable delay was included to support photographic evaluation. The unit was designed to have a high degree of flexibility to support the laboratory experiments since there was no way of predicting how the coating solutions would behave. Other operating parameters of the inkjet head were defined as follows:

- *Fluid Viscosity Range:* 20 to 100 cPs

- *Operating Temperature:* 23°C to 300°C

- *Operating Pressure:* Undefined. Enough pressure is needed to push viscous fluid through the nozzle size selected for the inkjet. May be operating at downstream pressures of 1100 psi (7.5 MPa) but this can be compensated for by adjusting the upstream pressure to keep the same pressure drop (a feature designed to facilitate integration with SCF processing equipment).

- *Droplet size:* The capability to make mono-disperse droplets in the 10 to 60 micron range.

Unfortunately, due to continued production problems, METSS never received delivery of the custom inkjet system to support the laboratory experiments. Instead, Codent provided METSS with one of their commercial P-9 units (an array of 9 nozzles, each 80 μm in diameter). This system was able to create droplets from solutions of the epoxy powder coating dissolved in acetone in concentrations from 5 to 25 wt% (higher concentrations were not attempted for fear of irreversibly clogging the unit). The results of these experiments are reported in Section 4.2.6. While these experiments produced very useful results, it should be pointed out that METSS had no control over the processing conditions of the polymer solutions. Therefore, it was not possible to optimize droplet generation by changing processing frequency, or the shape and amplitude of the pulse driving the piezoelectric crystal and hence control droplet size and distribution.

3.2.6.1 Acoustic Printing

During the course of the program, METSS identified a newly emerging printing technology that could be used to achieve the objectives of the program. This technology, termed *acoustic printing* was originally developed at Stanford, with support from Xerox, and is expected to be commercially available in the near future. While similar to inkjet printing, it offers significant advantages in terms of particle size control and hence printing resolution.

Dr. Richard Oeftering of NASA Lewis Research Center (NLRC) has investigated the use of acoustic printing methods to produce mono-disperse solder beads and agreed to work with METSS to test out the potential of using this technique to produce mono-disperse powders. A description of the acoustic printing process, the experiments performed with the support of NLRC, and the results of these experiments are presented in Section 4.2.6.1.

4.0 RESULTS

The results of the literature search, technical evaluation, and process evaluation efforts are presented in this section. All of the efforts described in Section 3.0 are addressed. However, under Section 4.2 (*Process Evaluation*), emphasis is placed on the processes that offered the most potential for achieving the technical objectives of the program. Thus, a preponderance of the information provided in the remainder of this report is related to the production of polymer particles using the GAS process and inkjet printing technologies.

4.1 Literature Search, Review, and Initial Technical Evaluation

In this section, the results of the literature search are briefly reviewed. A reference bibliography is provided in Appendix A by major field of inquiry. The results of the literature search were instrumental in allowing METSS to perform an initial technical evaluation of the proposed technologies to determine which techniques were more apt to yield positive results with respect to the program objectives. Furthermore, the literature review provided valuable information that was used to design the experimental procedures implemented under the program.

4.1.1 RESS

The literature related to the RESS process was fairly thorough and, when used in conjunction with the general literature on supercritical dissolution of polymers, provided the information needed to perform a technical assessment of this process. Most of the literature on RESS processing is related to the production of particles for the pharmaceutical industry. As a consequence, the literature reviewed was generally not applicable to the higher molecular weight resins systems of interest for the production of coating materials. However, even with the low molecular weight materials previously investigated there was a saturation limit of the materials being processed in the 1 to 3 wt% range, with most experimental results published related to solution concentrations of the order of a fraction of a percent. The main reason for this is the limited solubility of most materials in supercritical fluids and particularly in benign supercritical fluids such as carbon dioxide. A review of the general literature on the dissolution of polymers in supercritical fluids demonstrated the use of supercritical chlorofluoro-carbons may be used to dissolve some of the lower molecular weight polyolefins. However, this possibility was quickly ruled out as the commercial feasibility of scaling up such a process was highly improbable given today's environmental climate. As a consequence, experimental efforts related to the RESS process were limited.

4.1.2 GAS

The literature on gas anti-solvent (GAS) technologies was more limited than the literature on RESS processing as this technology is still in its infancy. The available literature was very instructive in terms of experimental set-up and identifying the processing variables of interest. However, once again, the literature was limited in its direct applicability to the program and the work published in this area ultimately proved to be of little value as it was limited to processing low molecular weight polymers (e.g., proteins and model compounds) and the models that were developed for GAS processing of these materials did not readily translate to the high molecular weight resins of interest to the current program. However, the basic literature was very instructive with regard to equipment development issues and processing variables that could affect the size, shape, and morphology of particles produced via this process.

Furthermore, the literature clearly demonstrated the superior aspects of GAS processing compared to RESS, particularly with regard to throughput and the ability to rely on the power of conventional solvents for polymer dissolution as opposed to supercritical fluids. However, for all practical purposes, this also means that the GAS process is limited to those polymers that are readily dissolved in environmentally friendly solvents. For the current program, GAS experiments were limited to epoxy resin systems dissolved in acetone and MEK.

4.1.3 SCF Processing of Polymers

A review of some of the general literature on supercritical fluid processing of polymers was performed to complement the RESS and GAS process evaluations. This literature review included a search for the supercritical fluid conditions needed to process the various coating resins of interest to the program, general literature on the development of supercritical fluid coating technology, and information on the influence of supercritical fluids on the spray atomization of coatings/resin systems. Union Carbide published heavily in this area to support marketing efforts associated with the development and introduction of the UNICARB® supercritical fluid coating process. However, published literature on the distribution of polymer droplets created by the UNICARB® spray process is limited to general comments on fan pattern with little information of droplet size and distribution. Ferro has performed some work related to this area with regard to the development of powder coatings using a supercritical CO_2 process. Ferro's process is discussed briefly in this section.

4.1.4 Inkjet

The literature on inkjet processing methods is quite extensive with regard to conventional printing processes, but limited with regard to the use of inkjet processing of high viscosity systems, i.e., polymer melts or solutions. Discussions with industrial contacts in the inkjet industry proved to be more fruitful in this area. One particular area of interest identified is the use of inkjet processes to produce micro-lens arrays and optical interconnects (of the order of 25 to 50 μm in diameter) from UV-curable acrylic resins and low viscosity thermoplastic resins. This work, performed by MicroFab, clearly demonstrated the potential of fabricating mono-disperse polymer droplets without the aid of solvents. MicroFab's work supports the technical feasibility of the proposed concept, demonstrating that the polymer droplets can be created under controlled conditions, i.e., conditions in which the inkjet device can be controlled precisely and a suitable resin formulation is available for processing.

The inkjet literature also produced several other results that could impact future program, including:

- the possibility of constructing piezoelectric pumps that essentially act as micro-dispensers of polymer melts to form droplets of a defined size

- recent developments in the area of *acoustic printing* - a technique where mono-disperse droplets are created by ejecting them from the surface of a liquid pool using a focused pulse from a piezoelectric transducer (droplet size can be controlled from 5 to 300 μm by simply changing the operating frequency of the piezoelectric crystal)

- a newly developed technology that facilitates the production of a large number of mono-disperse droplets using a micromachined array of transducers.

Each of these techniques offer some unique advantages that could impact the objectives of the current program and provide a possible vehicle for process commercialization. As a consequence of the literature search, METSS elected to investigate the use of acoustic printing methods to generate mono-disperse polymer beads with the assistance of Dr. Richard Oeftering at NASA-Lewis (Cleveland, OH). The results of this work are presented in this section.

4.2 Process Evaluation

The results of the process evaluation experiments are discussed in this section. Emphasis is placed on the processes that proved to be the most favorable for the production of pigmented polymer beads.

4.2.1 Materials Identification, Acquisition, and Qualification

As stated in Section 3.2.1, METSS elected to use pre-formulated powder coatings to support the process development efforts. A number of vendors were contacted to obtain sample materials to support the program efforts. At least one material from each category of interest was obtained to support the program efforts. A list of materials ordered to support the program is presented in Table 4.1.

Table 4.1. Powder Coating Materials.

Type	Supplier
PE	Thermoclad
PE	Quantum Chemical
PE (functionalized w/MAA)	PFS Thermoplastic
PP	Thermoclad
PVDF	Continental Coatings
PVC	Thermoclad
Nylon (78-1001)	Morton
Fluoropolymer (90-0000)	Morton
Polyester (20-1012)	Morton
Epoxy (10-1013)	Morton
Epoxy	O'Brien
Polyurethane	O'Brien

Most of the testing performed under the program involved the use of thermoset powder coating materials supplied by Morton and O'Brien. In order to ensure that the materials were processed in a safe range to avoid cure, METSS performed DSC experiments on each of these samples. The results of the DSC experiments are presented in Table 4.2. Three data points are presented for each sample: (1) the melting temperature of the powder; (2) the temperature at which unblocking occurs for cure to initiate; and (3) the exothermic peak associated with the curing process. In addition, since the RESS and SCF spray atomization experiments were performed with a low molecular weight polyethylene (2000 MFI) material

provided by Quantum and the Morton nylon, the melting points of these materials were also determined. All DSC measurements were performed at a scan rate of 10 °C/min.

Table 4.2. DSC Data

Polymer	Melting (°C)	Un-blocking (°C)	Cure (°C)
Epoxy (O'Brien)	63	83	159
Epoxy (Morton)	57	94	177
Polyurethane (O'Brien)	60	96	ND
Nylon (Morton)	187	NA	NA
Polyethylene	98	NA	NA

ND - not determined
NA - not applicable

Solubility limits and solution viscosity data were determined for the thermoset resins in various solvents as a function of concentration and temperature. The Morton Epoxy material turned out to be the easiest system to work with, so METSS elected to use this material as a *model* compound for the majority of the process evaluation experiments performed under this contract. For inkjet processing, the solution viscosity had to be less than 100 cPs. There were no set limits to the viscosity of the solutions used for the supercritical fluid processing experiments. However, since the flow rates under investigation were fairly high and the nozzle diameters were small, low viscosity solutions were desired. As it turned out, it was relatively easy to produce low viscosity epoxy solutions even at room temperature and high polymer concentrations. The 100 cPs room temperature viscosity requirements were met at solution concentrations of the order of 55 wt% for epoxy in acetone and MEK. Solution viscosity was readily reduced with slight increases in solution temperature, especially for the MEK solutions. A major difference between the solutions was the ability of the MEK to keep the pigments in the powder coating suspended in solution while they readily dropped out in the acetone mixture. Viscosity data curves are presented in Figure 4.1 for the epoxy powder coating in acetone and MEK as a function of polymer concentration and temperature.

4.2.2 Spray Drying

A laboratory spray drying system was developed to support the spray atomization experiments and inkjet processing. The design of the system was optimized using a 30% solution of epoxy in acetone. A vertical configuration standing about 6 feet tall with a heated air stream running parallel to the atomized spray worked best. This system provided a fine powder of paint at the exhaust side of the drying chamber. Since the atomized droplets used in the optimization of this design were much coarser and of larger volume than those that would be produced by the inkjet process, the design was thought to be robust enough for use in both experiments (i.e., spray atomization and inkjet processing). Difficulties with the supercritical fluid spray atomization process circumvented the need for the spray dryer to assist in these experiments. Furthermore, the design of the system turned out to be too robust to support the inkjet experiments, as the air flow through the system disrupted the recovery process. Droplet drying and recovery from the inkjet process was eventually performed using a straight section of tubing (approximately 30 inches in length) that was heated from the outside with an infrared

lamp. This provided enough heat and distance to facilitate full solvent evaporation from the droplets produced by the inkjet array.

4.2.3 Spray Atomization

There are a number of commercial spray atomization techniques capable of producing spherical particles, however the size distribution of particles produced by these processes is typically inversely proportional to product size. Thus, it might be possible to utilize some of these techniques to produce a tight distribution of 10 micron pigmented polymer beads, but the distribution of powders produced for HVTS applications would still be fairly broad. The only advantage over conventional powder coating production processes would be that the particles produced by atomization techniques would be spherical. Most of the work performed in this area of solid particle production is related to the atomization of metals and ceramics, with most of the continuing work related to the production of solder beads. With the exception of waxes, there appears to be very little available data on the production of spherical polymer powders of any substantial molecular weight. Thus this is an area that may be explored in more detail, particularly with the aid of ultrasonic techniques to assist the atomization process. However, atomization of polymer solutions poses several problems related to the viscoelastic nature of polymer solutions that have not been addressed by this community, including:

- local variations in the viscosity of polymer solutions
- variations caused by molecular weight distributions
- local fluctuations in flow rate.

Under the current program, METSS limited its process evaluation efforts to the application of supercritical fluid assisted spray atomization techniques. The SCF spray atomization experiments were designed to investigate whether or not the use of supercritical fluids in the spray atomization process created a narrow distribution of particle sizes that could be recovered for subsequent delivery via the HVTS process. The premise behind these experiments was the fact the spray pattern of the UNICARB® process is finer and more regular than the spray patterns produced by conventional spray coating processes. This has been attributed to the rapid evaporation of the supercritical CO_2 as it exits the nozzle with the resin system.

Two sets of experiments were performed under this effort using a number of approaches. However, neither of these experiments were successful. In the first set of experiments, performed using a modified ISCO lab scale SCF extractor, METSS was able to use supercritical CO_2 to dilute a polymer melt of low molecular weight polyethylene sufficiently to allow it to be sprayed though a 1/16 inch diameter tube. However, the resultant powder was coarse and irregular in size and shape and it was evident that atomization was not occurring. The addition of co-solvents to provide additional melt thinning did not seem to aid the process. Based on the results from the first set of experiments it was thought that that the process might be aided by the addition of melt mixing to ensure the supercritical CO_2 and co-solvents were thoroughly mixed with the polymer melt, thus driving the overall solution viscosity down to facilitate jet break-up and atomization. Thus, the experiments were transferred to a 1 liter, high pressure, stirred reactor. Experiments were performed with a number of different resins, including nylon, epoxy, and polyethylene. However, favorable results were still not achieved as the process was plagued by blow-by which made it impossible to achieve enough pressure to atomize the solution as it was pushed through the nozzle. This process was abandoned after a number of unsuccessful attempts,

which included several attempts to recreate the SCF process Ferro patented as an alternative method to produce powder coatings. Ferro's process simply involves the use of supercritical CO_2 as a diluent solvent to facilitate transport of a polymer melt through an orifice (250 to 2500 μm in diameter) where atomization occurs followed by rapid drying. Ferro claims their process produces a narrow distribution powder of the order of 40 μm in size. If this is indeed accurate, then Ferro's work supports our original hypothesis that this approach can be used to produce powders suitable for HVTS application. However, METSS could not reproduce these experiments to confirm Ferro's results.

4.2.4 RESS Processing

Only a limited number of RESS experiments were performed under the program. The primary reasons for this were: (1) the inability to dissolve any of the resin systems of interest in a suitable supercritical fluid under reasonable processing conditions; and (2) the solubility limits that could be achieved even under ideal conditions were too low to facilitate powder production at any appreciable level. A limited number of experiments were performed with low molecular weight polyethylene using supercritical CO_2, ethane, and propane to verify our initial technical assessment. None of these fluids exhibited a tendency to dissolve the polyethylene in an appreciable manner to facilitate subsequent precipitation during rapid expansion of the supercritical fluid.

4.2.5 GAS Processing

Simply stated, the GAS process involves the introduction of a solution into a pressurized chamber containing supercritical or subcritical fluid. The conditions of the fluid in the GAS chamber are optimized for interaction with the solvent in solution, causing the solvent to swell, thus creating a supersaturated solution from which precipitation of the solute proceeds. The high diffusivity of the supercritical fluid in the solvent facilitates rapid mixing and uniform precipitation of the solute from the supersaturated solution. The size of the solute particles is dictated by the rate of nucleation, the number of nucleation sites generated, and the concentration of the solute in the vicinity of the nucleation sites. These factors are in turn dictated by the concentration of solute in the solution, the rate of introduction of solution into the GAS chamber, and the GAS processing conditions.

The results of the GAS processing experiments are presented in this section. The results of the volume expansion experiments are presented first, followed by presentation of the acetone and MEK experiments. Pictorial references are provided in Appendix B to aid the presentation of the data. Exact processing conditions are provided in the figure captions. A summary of the experimental results is presented Section 5.0.

4.2.5.1 Solvent Expansion Experiments

In order to control the GAS processing experiments, it is important to understand the interaction of the solvent with the supercritical fluid, as the amount the supercritical fluid swells the solvent (i.e., the extent of supersaturation) ultimately controls the precipitation process (all other variables considered equal). Thus, METSS performed several solvent expansion experiments to investigate the effect of GAS processing conditions on particle nucleation and growth from the polymer solutions of interest. Solvents investigated included acetone, MEK, and methylene chloride.

Solvent expansion experiments were performed as follows:

- a known volume of solvent was introduced into the Jerguson gage and a baseline reading was taken of the solvent level through the sight glass

- CO_2 was introduced into the Jerguson gage and the system was allowed to equilibrate at pressure increments of 100 psi

- volume expansion readings were taken at each increment and plotted against CO_2 pressure.

The resultant volume expansion curves are presented in Figure 4.2. Acetone and MEK behaved in an almost identical manner, exhibiting gradual expansion to approximately 800 psi followed by increased expansion through the end of the experiments (1000 psi). Methylene chloride exhibited very little expansion at pressures below 800 psi, followed by a very sharp expansion at 800 psi. The large increases in volume correlated closely with the CO_2 phase change from gas to liquid. Additional experiments were performed to determine if the presence of solute atoms affected the experimental results, but no noticeable change in expansion behavior was demonstrated. The volume expansion measurements clearly indicate that rapid supersaturation occurs in solvent solutions of interest at pressures of the order of 800 to 900 psi CO_2. Thus, it may be hypothesized that small uniform particle generation will be favored by GAS processing at pressures above this range. From the shapes of the acetone and MEK curves, it also appears that at pressures below this range, there may be a substantial change in formation of particles as a function of GAS processing conditions. However, it should be noted that the nature of the experiments performed does not provide any insight into the rate of mixing and subsequent rate of volume expansion as all measurements were taken under equilibrium conditions. Thus, it is possible that there are significant differences in the rate of expansion between acetone and MEK upon mixing with CO_2. In fact, significant differences may be expected based on the vast differences in the rate of evaporation of acetone relative to MEK (acetone evaporating more rapidly).

4.2.5.2 GAS Experiments

The Morton epoxy powder coating was used in all of the GAS processing experiments at a number of different concentration levels ranging from 2.5 to 25 wt%. Due to the length of the experiments, testing was limited to MEK and acetone solutions, as these solvents are better suited for large scale production. Experimental conditions (see Section 3.2.5) were varied systematically in an attempt to optimize process conditions to produce polymer beads in the size range of interest.

Initial GAS experiments were performed in a Jerguson gage so the precipitation process could be visually monitored. Mixing, nucleation, and precipitation processes were clearly evident with the introduction of the polymer solution into the Jerguson gage (although the process occurred too rapidly for any distinguishing features to be noted). In an effort to slow this process down, some attempts were made to reverse the process by starting the experiment with the polymer solution in the Jerguson gage and incrementally pressurizing the gage with CO_2. However, these experiments provided no additional insights.

After the initial experiments with the Jerguson gage, the GAS experiments were shifted to a 2.75 liter high pressure vessel that allowed for a substantial volume of material to be processed. All experiments were performed under a constant flow of CO_2 into and out of the processing vessel, with flows running co-current or counter-current to the solution as it was introduced into the GAS chamber. An SEM picture of the epoxy powder prior to dissolution and GAS processing is provided in Figure 4.3.

The effect of polymer concentration in solution with acetone is demonstrated in Figure 4.4. Two general trends can be noted:

1. the morphology of the processed powder changes from a combination of rods and spheres, to spheres (albeit spheres that are coalesced) as the concentration of polymer decreases from 25 to 2.5 wt% polymer in solution

2. the size of the spheres demonstrated a tendency to increase in size as the solution concentration of polymer decreases, demonstrating increased time for growth or coalescence.

This first set of figures demonstrates the main obstacles the rest of the GAS experiments performed under the program were designed to overcome:

- production of spherical morphologies with no rods present

- maximizing the growth of the spherical particles formed

- identifying processing conditions that limited or controlled particle coalescence and facilitated dry powder production.

In conjunction with changing processing conditions, it was thought that the use of surfactants could help overcome these obstacles. While this introduced another variable into an already complex equation, these experiments were met with favorable results. Figure 4.5 demonstrates the effect of a small amount of surfactant (0.01% Pluronic R-17) on particle morphology under identical processing conditions. While the particles produced continued to agglomerate, they were all spherical and slightly larger than those produced without surfactant. These results clearly indicate the importance of surface tension on the outcome of polymer morphology. Attempts made to optimize surfactant effects were met with limited success due to the number of other variables of interest and limitations imposed by the scope of the current program.

One of the most surprising results of the GAS experiments was the effect on particle morphology of the direction of CO_2 flow relative the direction of the input solution flow stream. Counter-current CO_2 flow rates consistently generated particle morphologies that were more clearly defined, with less agglomeration of particles and a more uniform distribution in the size of the independent spherical particles created. This effect is demonstrated in Figure 4.6. The processing conditions in Figure 4.6 are identical, with the flow in (a) running co-current and the flow in (b) running counter-current. Although this hypothesis was not tested, the results indicate that the generation of well defined spherical particles may be improved with mixing.

Next, the effect of pressure in the GAS processing vessel were investigated. As previously discussed, acetone exhibits a gradual increase in volume with CO_2 pressure up to 800 to 900

psi, where it exhibits a rapid expansion to its maximum (at least measurable) level, after which further increases in CO_2 are ineffectual. The GAS process works on the principle of instantaneous supersaturation. Thus, the rapid expansion of acetone with CO_2 mixing at pressures above 800 to 900 psi is desirable. From a processing standpoint, lower pressures are preferred if the same results can be generated. Thus, several experiments were performed to evaluate the effects of processing the same polymer solution at 900 psi and 1400 psi, all other conditions being the same. The results of these experiments are presented in Figure 4.7, where the production of rods at lower pressures is clearly evident.. These experiments demonstrate that polymer morphology can be a function of GAS processing pressure, even if the pressures used are in the range for maximum solvent swelling. This difference may be attributed to a number of factors, including:

- the change in the rate of mixing and swelling as a function of CO_2 pressure
- the change in density of CO_2 with pressure
- the change in pressure drop across the nozzle.

The effect of pressure drop across the nozzle was tested at 900 psi by performing identical GAS experiments with two different nozzles (Figure 4.8), one nozzle 180 μm in diameter, the other 760 μm (feed tube diameter with no nozzle). The results were very interesting as the solution introduced though the larger diameter nozzle (b) did not create any rods in the final product. The implications of this are important, as it demonstrates that the GAS process is dominated by a nucleation, precipitation, and growth mechanism and that jet break-up does not influence particle morphology. However, the creation of a jet stream of concentrated polymer solution can be detrimental to the production of spherical particles as the rapid expansion of solvent in the jet in the presence of the high polymer concentration solution can lead to rod formation as the geometry of the jet stream is essentially *frozen* into place as it passes through the nozzle.

Results of the GAS experiments performed with MEK are presented in Figures 4.9 through 4.11. One of the most interesting things to note in the MEK experiments is the absence of rod formation, regardless of polymer concentration, GAS chamber pressure, or nozzle diameter. Figure 4.9 shows the results of two identical runs with the exception of the solvent used in each run. Both are low pressure (900 psi), low concentration (2.5 wt% polymer). In the acetone run (a) there is clear evidence of rods. In the MEK run (b), no rods are present. Another interesting point to note in these pictures is the size of the particles created in the MEK run are significantly smaller than the particles created from acetone. The absence of the rods would suggest that nucleation and precipitation occurred at a slower rate (i.e., the jet of polymer solution was not precipitated at the nozzle, subsequently leading to rod formation). The smaller particles may indicate more intimate mixing between the polymer solution and the CO_2 leading to the generation of more nucleation sites and smaller particles at supersaturation.

In Figure 4.10(a), a 10% solution in MEK is processed at 1400 psi, with no rods present. However, an even more dramatic demonstration of the difference in behavior between acetone and MEK in the GAS experiments is demonstrated in Figure 4.10(b), where the concentration of polymer in MEK is 25% and the GAS processing pressure is 900 psi with no rod formation noted in the powder recovered. Two other significant feature of 4.10(b), are:

- the size of some of the particles produced is approaching 5 μm

- the appearance of pigment particles protruding through the surface of the polymer particles clearly demonstrates an encapsulated morphology.

Another demonstration of the effects of co-current versus counter-current flow is provided in Figure 4.11, with MEK as the solvent. Once again, more clearly defined particles were produced under counter-current flow conditions and particle agglomeration is less prevalent with counter-current flow. However, an additional point noted in the MEK experiments is the larger size of the particles formed under counter-current flow conditions. This effect may be attributed to a difference in nucleation and growth behavior under counter-current conditions, or the possibility also exists that existing particles may continue to grow under counter-current flow conditions at the expense of new particle formation and growth. However, there is no experimental basis to support either of these arguments or to rule out the existence of other possibilities.

The final figure (4.12) demonstrates the capabilities of using GAS processing techniques to create vesiculated morphologies. This particular picture is of a polycarbonate sample, that was dissolved in NMP and processed at 1100 psi through a 760 micron nozzle. The rod-like structure is obviously very hollow with a honeycomb-like structure exhibiting large voids in a porous membrane of polymer. Vesiculated morphologies may be created by introducing a sharp pressure drop during processing, or by mixing supercritical CO_2 with the input stream.

4.2.6 Inkjet Results

The results of the inkjet processing experiments are presented in Figures 4.13 through 4.16. All of the figures represent polymer beads formed from solutions of epoxy in acetone under identical processing conditions. The only variable across the experimental results presented is the concentration of epoxy in solution. Only the supernatant liquid was processed to avoid clogging the inkjet with pigment. Figures 4.13 and 4.14 are presented at a magnification of 500X with a 60 μm scale for the 5 wt% and 10 wt% polymer solution concentrations respectively. Figures 4.15 and 4.16 are presented at a magnification of 300X with a 100 μm scale for 20 wt% and 25 wt% epoxy solutions. Particle agglomeration and size both showed a tendency to increase with polymer concentration.

The inkjet process proved to be a very successful vehicle for creating polymer beads. From an inkjet droplet production standpoint, one of the most interesting features worth noting in the SEM pictures of the polymer beads is the distribution in the size of the particles produced. The fact that the particles created using the 10 wt% (Figure 4.14) solution are essentially bi-modal in distribution is especially interesting. The distribution in particle sizes may be attributed to several factors:

- local variations in solution viscosity during droplet formation

- non-uniform solvent evaporation

- local variation in droplet production from nozzle to nozzle in the inkjet array (although this particular print head is supposedly optimized to eliminate this effect)

- satellite production as a consequence of improper process settings for the solutions being tested.

While the contribution of the first two factors can not be ruled out for the 5, 20, and 25 wt% solutions, the uniformity of the particles formed from the 10% solution demonstrates the commercial settings on the inkjet system were close to ideal for the production of uniform satellites (approximately 25 μm in diameter) created during the production of the primary polymer droplet. This would most likely mean that the original droplets were also uniform in size, but this is not supported by the particles shown in Figure 4.14. Thus, other factors may also be contributing to the final size of the polymer droplets. The implications of this are important however, as it does imply that controlled satellite formation is possible and this may provide a viable route for the production of small diameter HVTS powders (with one classification step) or the production of pigmented polymer beads.

An interesting feature in all of the SEM pictures of the polymer beads is the obvious formation of hollow core beads through the inkjet process, at least for the large particles produced. It is not readily clear whether the smaller particles (less than 25 μm) are solid or hollow core, although they all appear to be solid spheres. The presence of the hollow core spheres is not surprising as the size of the droplets and the fast evaporation rate of acetone would be expected to lead to rapid mass transport of the solvent from the surface of the droplet, creating a solidified shell that ultimately defines the diameter of the polymer sphere. Subsequent processing efforts should include formulation modification efforts that incorporate a fraction of slow and medium drying solvents that allow the outer structure to stay *open* long enough for all of the fast drying solvents to flash off before solidification begins to occur. The balance of the solvent blend may be adjusted to control the overall size of the polymer beads created, the creation of hollow core or solid polymer beads, and the thickness of the outer shell in the hollow core beads. Thus, formulation modification efforts will not only make it possible to control the size of the polymer beads created, but also their bulk density. As inkjet droplet production methods are strongly influenced by surface tension effects, the use of surfactants should also be investigated.

It should be noted that the destruction of the hollow core polymer beads may be attributed to post process handling, as the polymer samples were transported for SEM analysis between two glass microscope slides. However, it is also possible that some of the spheres exploded as trapped solvent tried to escape the hard shell of the polymer bead. In future efforts polymer bead samples should be deposited directly on conductive tape for subsequent SEM analysis.

4.2.6.1 Acoustic Printing Results

Acoustic printing experiments were performed at NLRC in conjunction with Dr. Richard Oeftering. In acoustic printing, a piezoelectric crystal is placed beneath the surface of a liquid. The acoustic wave created by the piezoelectric is focused at the surface of the liquid and the kinetic energy created by the pressure wave causes the droplet to be ejected from the surface. The diameter of the drops can be readily changed by changing the processing frequency.

METSS provided NLRC with a number of polymer solutions to investigate the applicability of acoustic printing technology to the production of mono-disperse polymer beads. Originally, METSS provided samples of polyurethane in MEK at concentration levels from 30 to 50 wt%. These samples were tested, but the results were unsuccessful. However, a second series of experiments were performed with solutions of epoxy in acetone at concentrations up to 30 wt%. These experiments were very successful, clearly demonstrating the potential of this technique to produce mono-disperse droplets from a 30% solids solution with pigment. The

drops produced were large (calculated at 120 μm) but extremely uniform (Figure 4.17). No attempts were made to change the diameter of the drops by increasing the operating frequency, as there was a flaw in the crystal being used to produce the acoustic energy, and higher operating frequencies could have lead to its destruction.

5.0 CONCLUSIONS

The project, as it was entered into, was very ambitious as it was the overall objective of this program not only to identify technologies to produce mono-disperse polymer powders, but to provide sufficient quantities of materials for further testing and evaluation by the Air Force. This not only included materials for application by the HVTS process, but also pigmented polymer beads for testing and evaluation in high performance aircraft top-coat formulations. While the program did not meet this objective, some very significant strides were made toward this goal and some very interesting advances were made in the area of polymer processing. Specifically, METSS was able to accomplish three things under this program that have not been previously performed:

1. METSS was able to produce micron scale polymer beads from solutions containing high molecular weight resins via the GAS process.

2. The ability of using acoustic printing methods to produce mono-disperse droplets from a high molecular weight polymer solution was demonstrated for the first time.

3. METSS was able to produce and collect spheres of epoxy powder coating from a polymer solution processed using commercial inkjet equipment.

5.1 Process Summaries

Some concluding remarks and suggestions for future research are presented by technology area in the remainder of this section.

5.1.1 Spray Atomization

Ferro Corporation has reported the production of mono-disperse 40 micron powder coatings by a melt-spray atomization process assisted by supercritical CO_2. If the particles produced by this process are indeed mono-disperse, then the process developed by Ferro may provide a viable means of producing powders for HVTS. However, due to the number of other variables involved, it is difficult to believe that the powders produced are indeed mono-disperse. Thus, it would be important to obtain a sample of these materials and perform particles size analysis on them to determine if further work is merited. If the particles are not uniform in size, then it may be worth while to attempt this process using an acoustic nozzle to assist droplet formation. With this possible exception, it is our opinion that the desired particles can not be produced by existing atomization processes.

5.1.2 RESS Processing

The utility of RESS processing is limited with regard to the current application due to the following factors:

- an inability to dissolve any of the resin systems of interest in a suitable supercritical fluid under reasonable processing conditions

- the solubility limits (weight percent polymer in solution) that may be achieved even under ideal SCF processing

- the cost of implementing this technology in the low margin coatings market would be prohibitive.

No further RESS processing work is recommended.

5.1.3 GAS Processing

Currently, it appears that the capability of using GAS processing techniques to create mono-disperse polymer beads of the size range needed for HVTS coatings (20 to 60 μm) is limited. However, based on the work performed under this program it does appear to be technically feasible to use GAS processing to create pigmented polymer beads which may be used in the formulation of durable, cleanable coatings for improved service life.

Figure 5.1 provides a pictorial description of the progress METSS made during the course of the program optimizing GAS processing conditions to produce spherical polymer beads, demonstrating the transition in powder morphology from rods (a) to spheres (b) as processing conditions were optimized through repetitive testing and evaluation. The progress METSS made in this area is significant as METSS is the first group to address the challenge of creating spherical particles from high molecular weight polymer solutions using GAS processing technology. During the course of this program, METSS was able to identify the key processing variables that favored the production of spherical polymer beads, including:

- low solution concentrations*
- lower processing rates (in-flow of polymer solution)*
- larger diameter nozzles
- the use of surfactants
- higher processing pressures*
- counter-current flow.

Furthermore, by comparing the results of the acetone and MEK experiments, METSS was able to demonstrate that polymer bead processing was favored by the use of slower evaporating solvents. Furthermore, it appears that the use of slower evaporating solvents may facilitate the use of more favorable processing conditions (lower pressures*) and improve processing efficiency by allowing higher concentration solutions* to be processed at higher through-put rates*.

The results of the GAS processing experiments were very encouraging. This process merits further investigation as it does appear that GAS processing techniques can be used to effectively create pigmented polymer beads for advanced coatings. Production criteria should be reviewed prior to further work, as pigment packing and ultimate performance is favored by spherical geometry's. These properties are not typically favored by the use of mono-disperse particles, but by a distribution in particles size. Thus, the necessity of creating mono-disperse pigmented polymer beads for durable, cleanable coatings should be evaluated before proceeding further with these efforts. The possibility of using a distribution of spherical particles in the formulation of these advanced coatings will significantly impact the amount of technical effort required to reach this objective. Furthermore, the particle size range of interest

should also be re-evaluated, as particles smaller than 10 μm in diameter may actually provide better overall performance in the desired application. Based on current results, particles diameters in the 1 to 5 micron range may be readily achieved.

As a final issue, the overall economics of using GAS processing for HVTS powder coating production or the processing of pigmented polymers beads will have to be evaluated in terms of total life-cycle costs. At this time, there is no way to estimate the cost of creating pigmented polymer beads using GAS processing techniques, the impact of this cost on the cost of the coating formulations developed using these particles, or the life-cycle cost savings incurred to by use of these new high performance coatings.

5.1.4 Inkjet Printing

While progress on the inkjet printing experiments was severely hampered by the problems encountered in the development and delivery of the custom inkjet print system being provided by Codent (UK), some significant strides were made using a commercial unit that demonstrates the technical feasibility of using this approach to process powders suitable for HVTS application.

In summary, METSS was able to create spherical powders of epoxy powder coating from acetone solutions containing from 5 to 25 weight percent polymer. While the distribution of particles created by this process was not mono-disperse, the results are still very encouraging as spherical particles were able to be produced using the factory settings on the inkjet system. With proper control over the inkjet processing variables (e.g., frequency, pulse amplitude, pulse duration, and shape) METSS should be able to optimize the processing conditions for the specific solution being processed to generate a mono-disperse powder. Ultimate particle size will be dictated by the inkjet production variables, the characteristics of the polymer solution being processed, and particle drying/collection methods.

With additional work, METSS should be able to successfully adapt the inkjet process to create mono-disperse polymer beads in the 20 to 60 micron range for HVTS application. It may also be possible to create pigmented polymer beads of the order of 10 μm in diameter using inkjet technologies and one of two approaches:

- the use of very low solids solutions and proper control over drying conditions

- by the controlled production of satellite droplets (small droplets that form in conjunction with main droplet production), followed by separation and drying, or downstream classification.

Technical experts at Codent believe controlled production of satellite droplets may provide a viable approach to using inkjet technologies to create particles in the size range of interest for pigmented polymer beads. However, the production of 10 micron particles would be significantly more challenging and require the use of high speed photographic techniques to support the process development efforts.

The use of a larger inkjet array would be desired to improve process through-put, and particle drying and collection methods would have to be optimized accordingly. With the assistance of Codent, it will be possible to adapt the commercial P-9 head with the variable controller built

during the course of this program to achieve the control over the processing variables. This will provide the quickest route to success, in lieu of the continued efforts to build an integrated custom production unit. The variable control unit does have an integrated strobe to facilitate photographic interrogation of the droplet production process.

All subsequent inkjet processing efforts should be strongly linked to formulation development efforts, as the correct blend of solvents is critical to the controlled formation of polymer beads. The balance of the solvent blend may be adjusted to control the overall size of the polymer beads created, the creation of hollow core or solid polymer beads, and the thickness of the outer shell in the hollow core beads. Thus, formulation modification efforts will not only make it possible to control the size of the polymer beads created, but also their bulk density. This last factor has an obvious (and very favorable) impact on the production of pigmented polymer beads by inkjet processing techniques for advanced coating formulations.

5.1.5 Acoustic Printing

The preliminary results achieved under this program clearly demonstrated the capability of using acoustic printing methods to produce large mono-disperse droplets from a 30 wt% solution of a commercial epoxy powder coating in acetone. Other works have already demonstrated the potential of using this technology to produce mono-disperse droplets from 300 μm in diameter down to 5 μm simply by increasing the operating frequency of the crystal and re-focusing the beam at the surface of the liquid. Thus, this technology potentially may be used to produce 20 to 60 micron HVTS coatings as well as 10 micron pigmented polymer beads. The one possible limitation would be the direct production of vesiculated polymer beads. However, there is no reason to believe that the factors controlling the formation of hollow core polymer beads in the inkjet process will not impact the production of polymer beads by acoustic printing methods. Therefore, acoustic printing methods should also be complemented by solution formulation efforts to gain precise control over particle formation geometry. Post processing with supercritical CO_2 may also be used to change the bulk density of the resultant polymer beads (see Figure 4.12). Other efforts that would have to be performed to support this technology would be the development of an appropriate means of collecting and drying the droplets as they are ejected from the surface of the polymer solution. However, there are commercially available means of achieving this task that are currently being used in commercial particle atomization processes.

As far as process commercialization is concerned, METSS believes that ongoing advances in the printing industry will make this approach commercially feasible for large scale production. Xerox has already demonstrated the potential of using this technology to produce photo quality prints using array technology to get the desired throughput for printing operations. Furthermore, the array device fabricated by Xerox for their prototype development efforts included a mechanism to automatically control the height of the liquid pool at the focal point of the acoustic energy, which is a primary requirement for droplet production via this technique. Thus, two of the major technical challenges associated with the transition of this technology to the field have already been addressed.

5.2   Final Recommendations

Based on the efforts performed under this program, METSS recommends the Air Force pursue the following:

- further development of GAS processing techniques for the production of pigmented polymer beads

- further development of inkjet processing techniques (including acoustic printing methods) for controlled production of mono-disperse powder coatings for HVTS application and the production of pigmented polymer beads

- formulation development work to support GAS and inkjet processing efforts, with a specific emphasis on controlling solvent blends and surfactant concentrations for the creation of solid and hollow core polymer beads.

APPENDIX A

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APPENDIX B

REPORT FIGURES
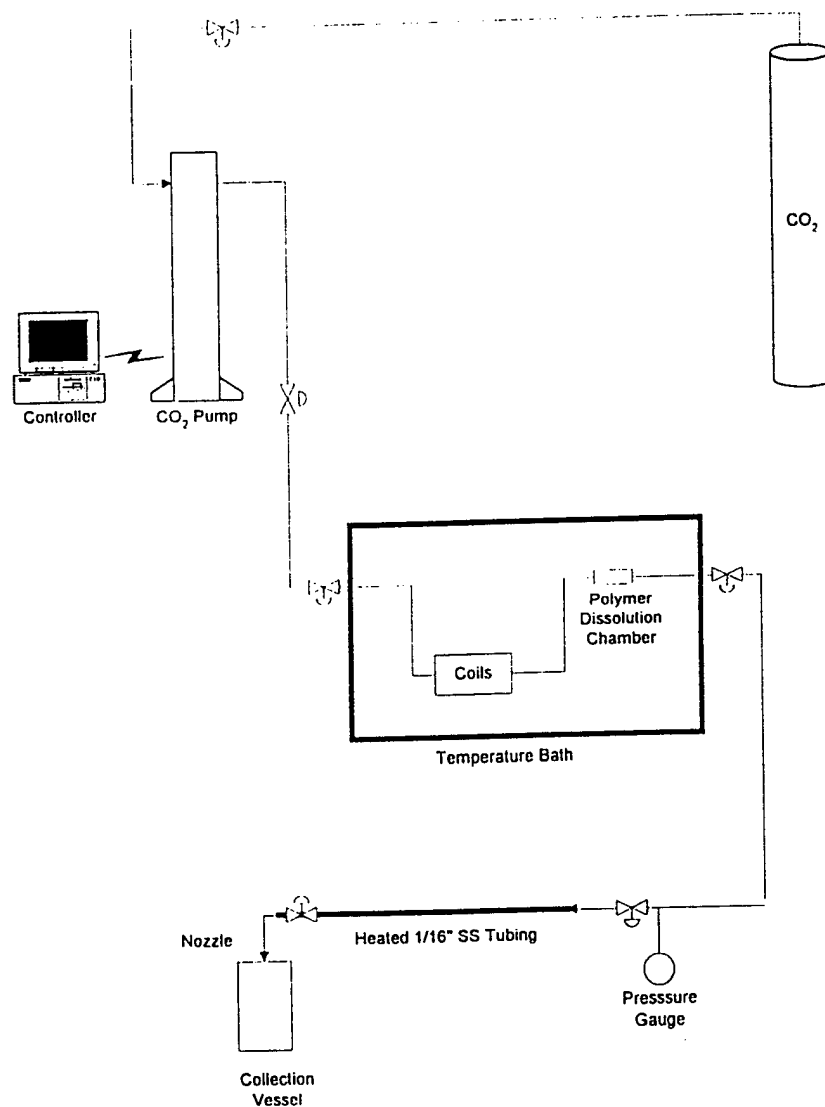
Figure 3.1. RESS process schematic.

CO$_2$

Solution Reservoir

Solution Pump

CO$_2$ Pump

Presssure Gauge

Controller

CO$_2$ / Solvent

SFE Tank

(b)

CO$_2$

Solution Reservoir

Solution Pump

CO$_2$ / Solvent

SFE Tank

CO$_2$ Pump

Presssure Gauge

Controller

(a)
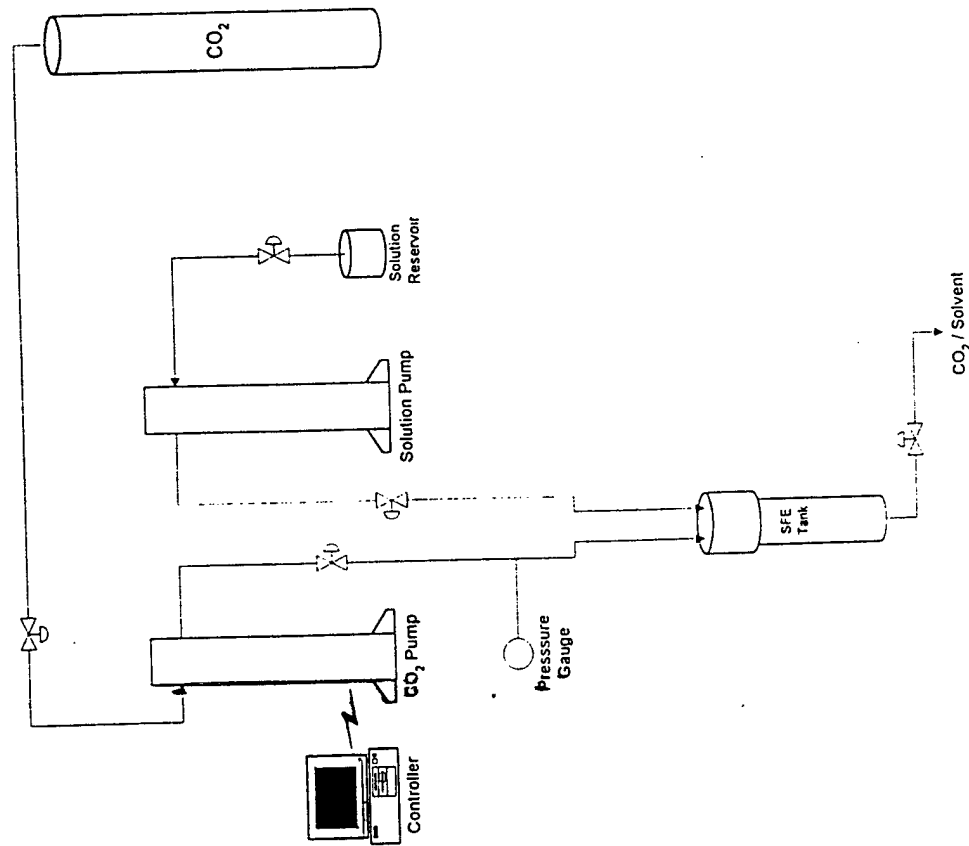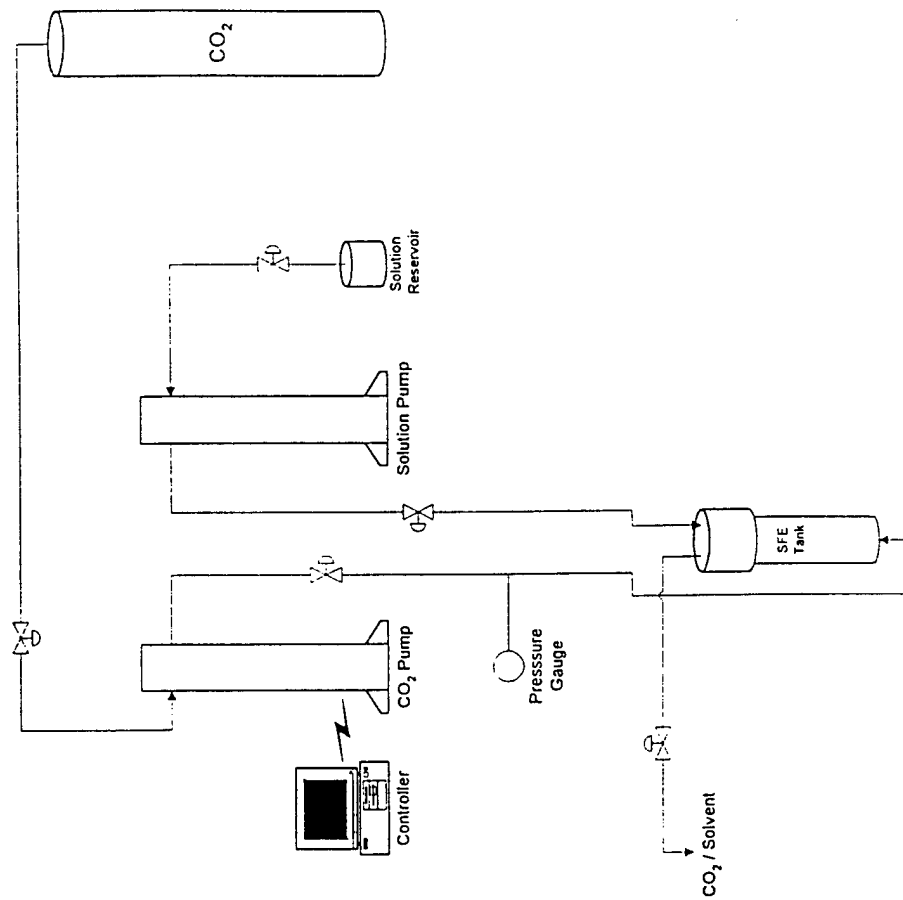
Figure 3.2. GAS process schematic: (a) co-current CO$_2$ flow; (b) counter current CO$_2$ flow.
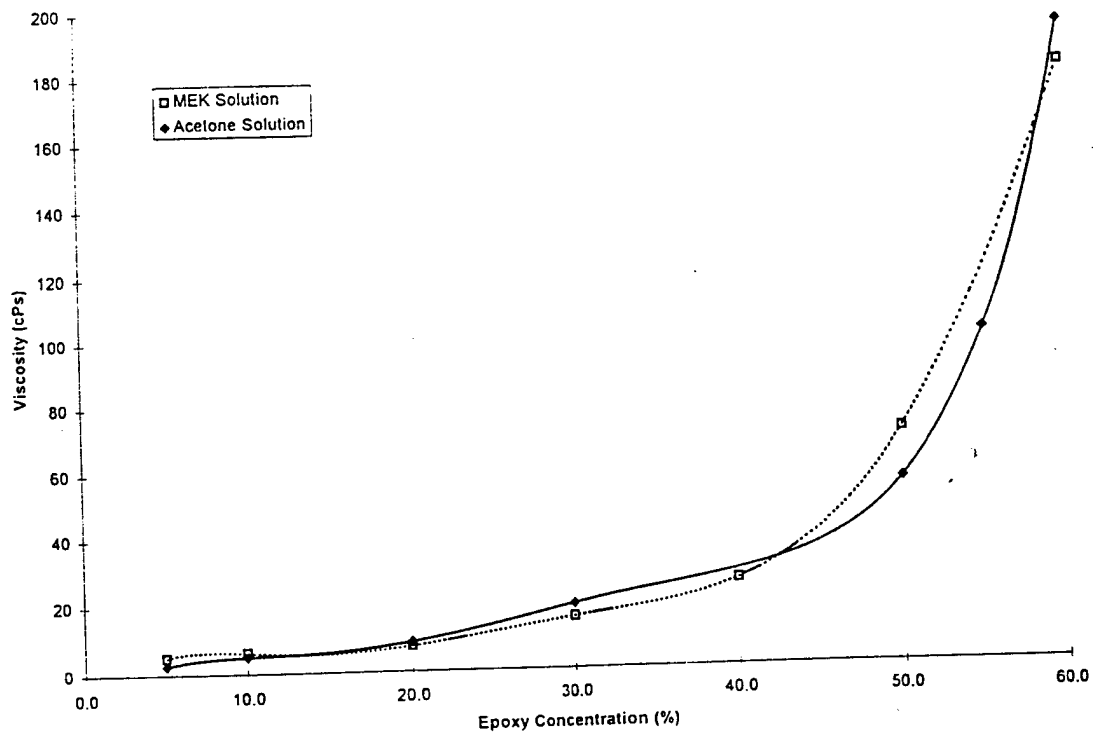
(a)

60% Epoxy Solutions
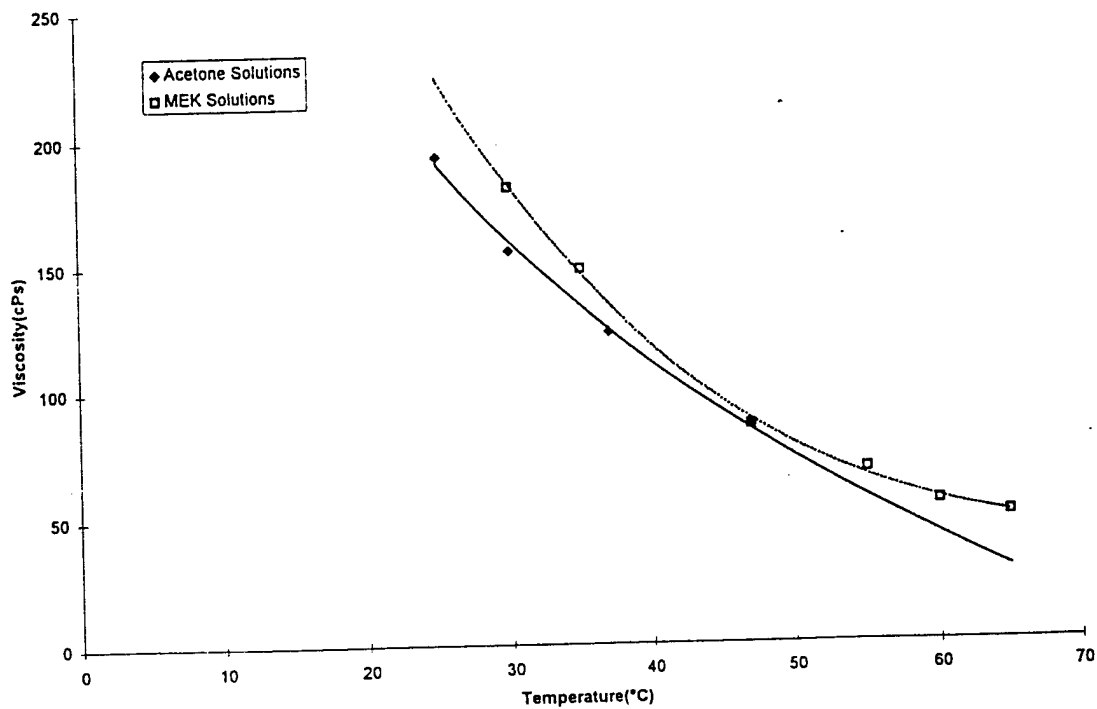
(b)

Figure 4.1. Solution viscosity data curves presented as a function of polymer concentration (a) and temperature (b).

Chart1
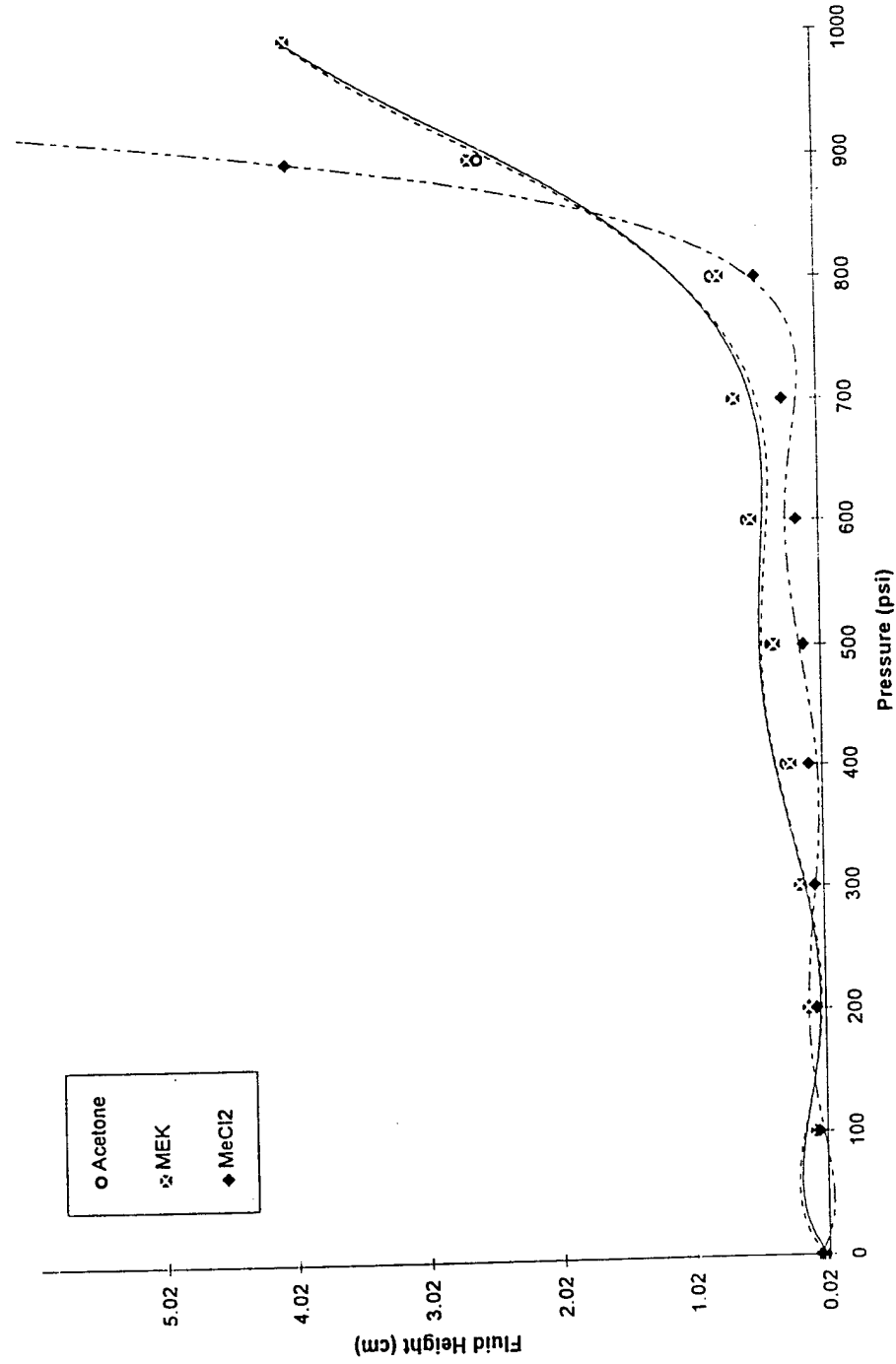
Figure 4.2. Equilibrium solvent expansion curves as a function of CO_2 pressure.

METSS Final Report: F33615-94-C-5803, Task Order No. 14
Appendix B
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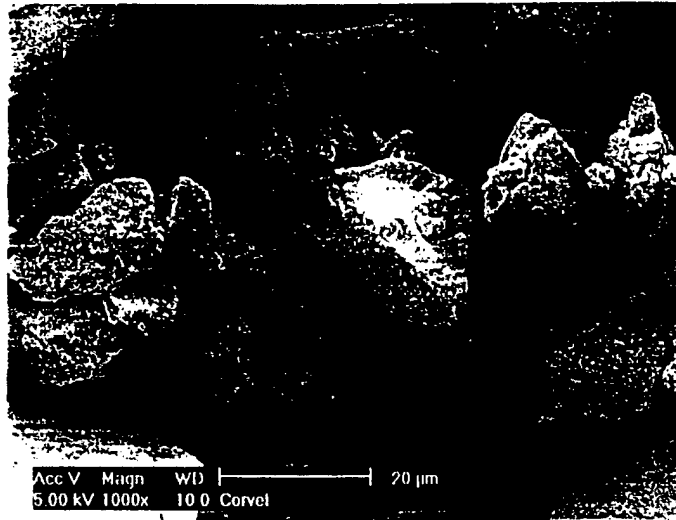
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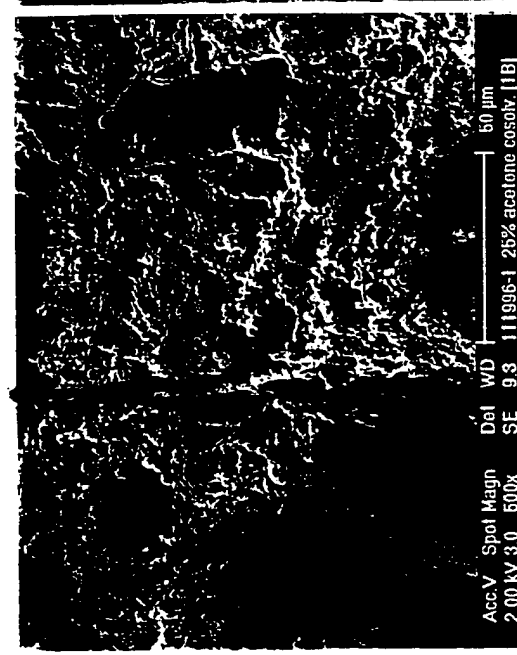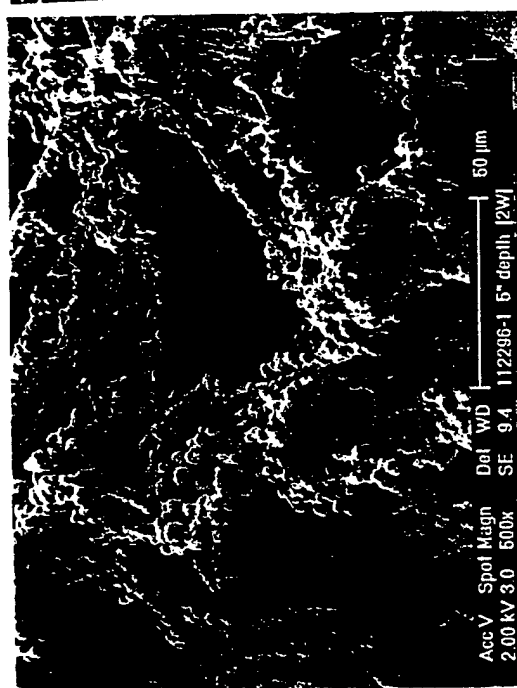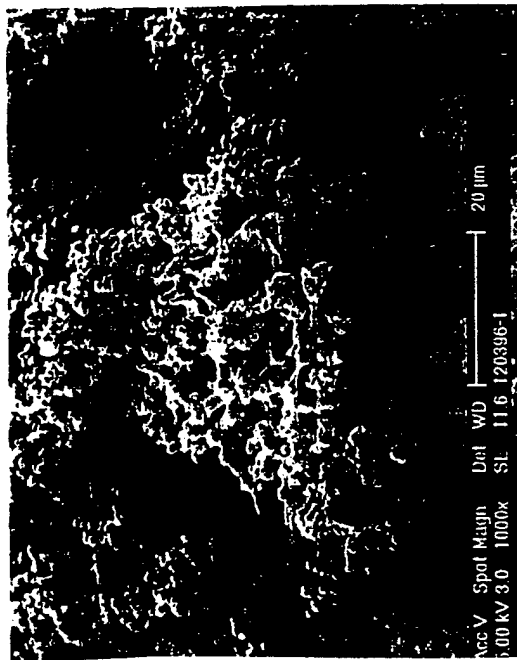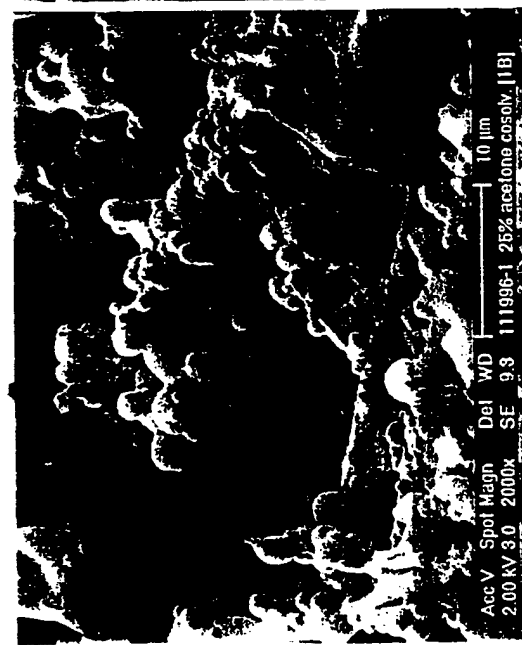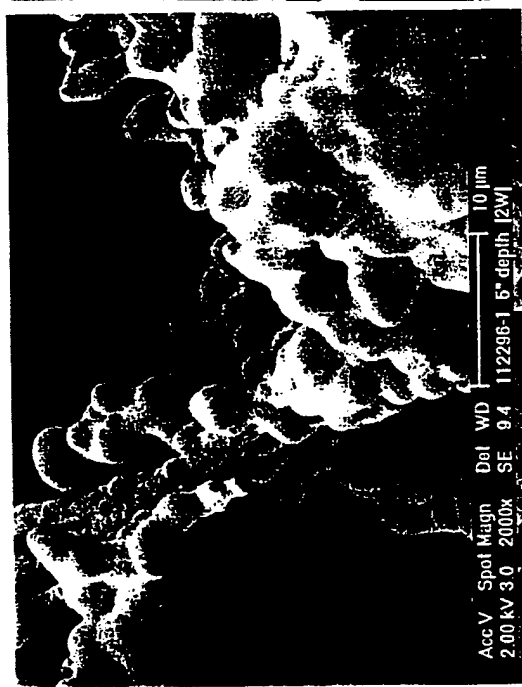
Figure 4.4. Effects of polymer concentration on GAS processing results: (a) 25 wt% polymer in acetone; (b) 5 wt%; (c) 2.5 wt%. GAS processing conditions: 1400 psi; 150 µm nozzle; co-current CO_2 flow; 5 ml/min - 10 min; no surfactant.
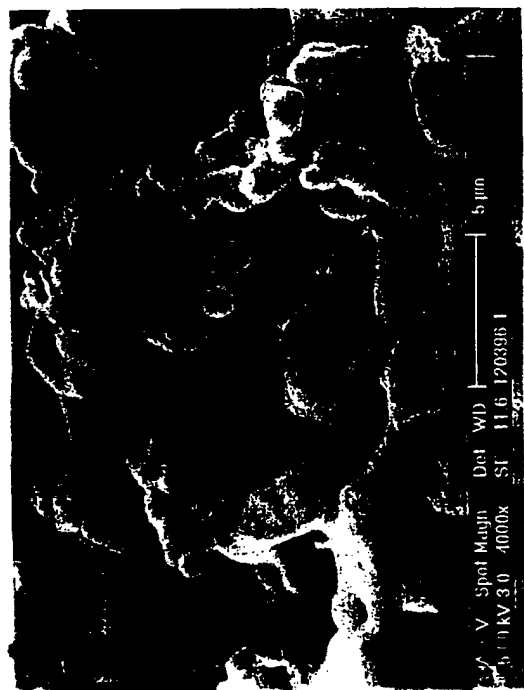
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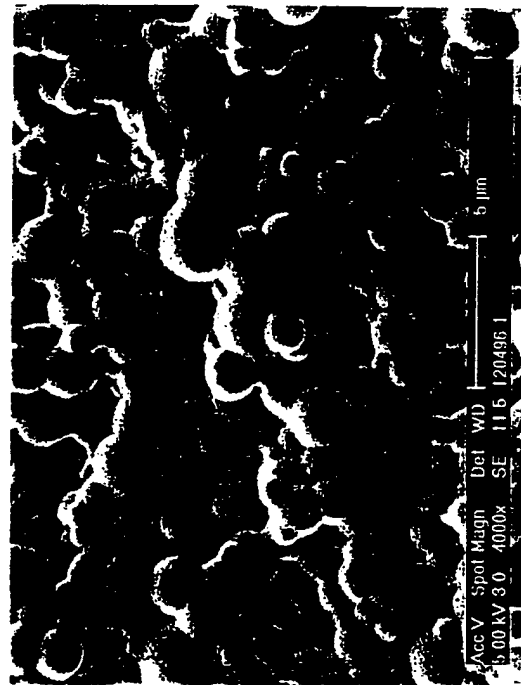
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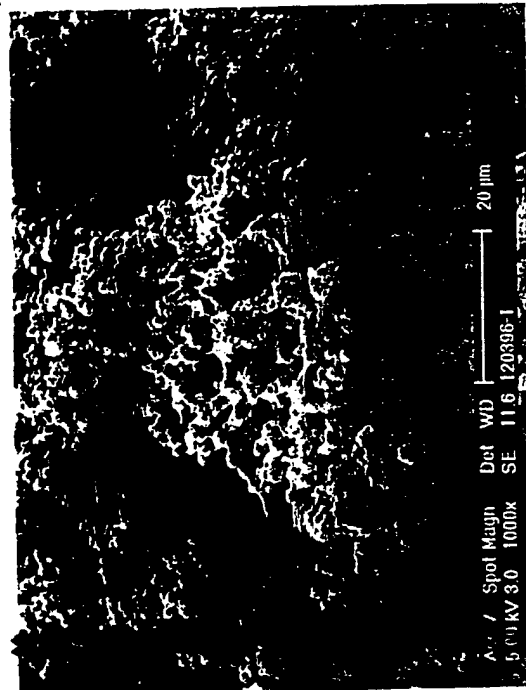
Figure **4.5.** The effect of surfactant on GAS processing results: (a) no surfactants; (b) 0.01 wt% Pluronic R-17. GAS processing conditions: 2.5% epoxy in acetone; 1400 psi; 150 μm nozzle; co-current CO_2 flow; 5 ml/min – 10 min.
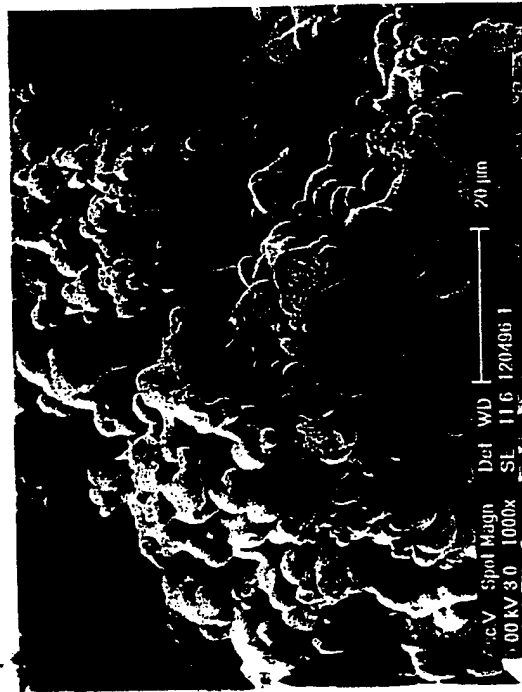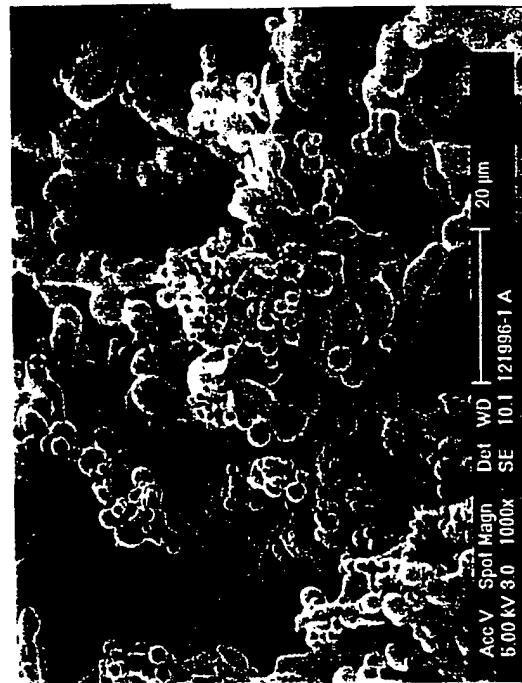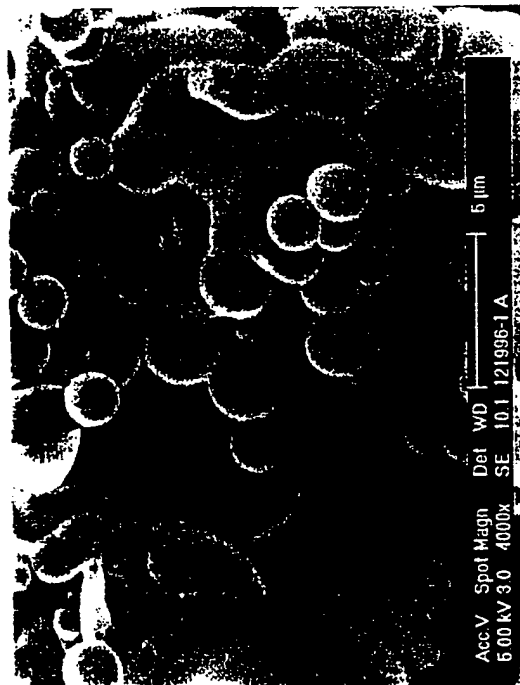
Figure 4.6. Effects of CO$_2$ flow direction on GAS processing results: (a) co-current flow; (b) counter-current flow. GAS processing conditions: 2.5% epoxy in acetone; 1400 psi; 180 μm. nozzle; 5 ml/min - 10 min; 0.01 wt% Pluronic R-17.
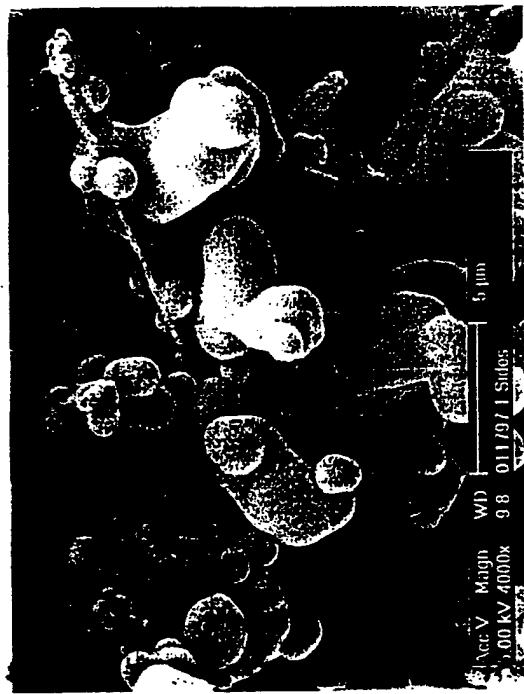
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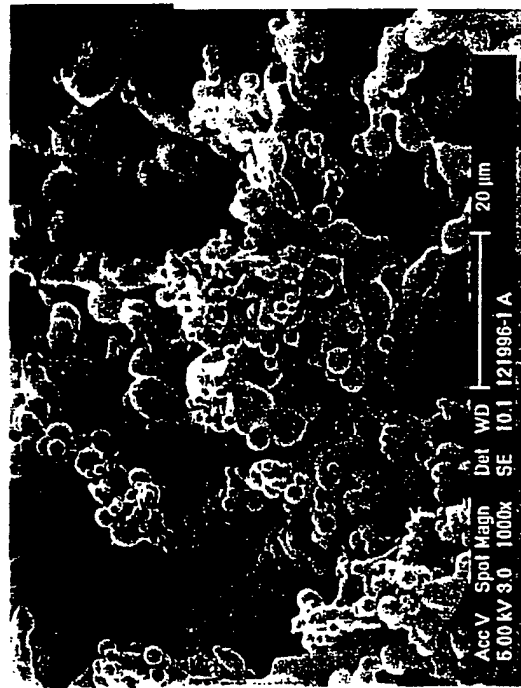
(b)

Figure 4.7. Effects of GAS processing pressure on particle morphology: (a) 900 psi; (b) 1400 psi.
GAS processing conditions: 2.5% epoxy in acetone; 180 μm nozzle; counter flow; 5 ml/min – 10 min; 0.02/0.01 wt% Pluronic.
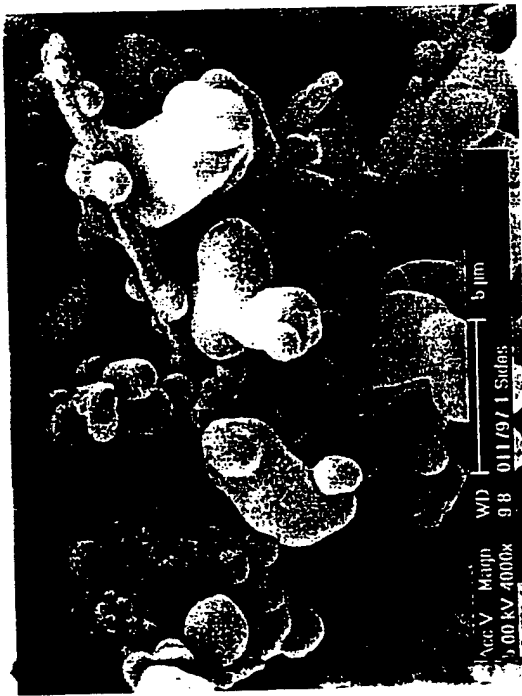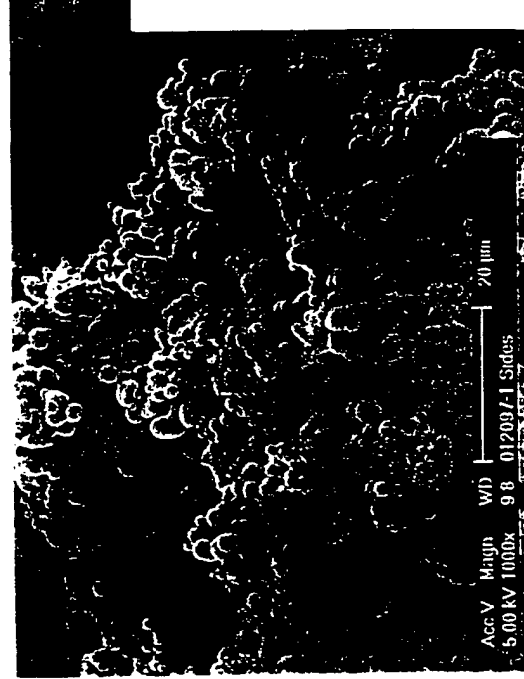
Figure 4.8. Effects of nozzle size on GAS processing results: (a) 180 μm nozzle; (b) 760 μm nozzle. GAS processing conditions: 2.5% epoxy in acetone; 900 psi; counter flow; 5 ml/min - 5 min; 0.02 wt% Pluronic.

METSS Final Report: F33615-94-C-5803, Task Order No. 14
Appendix B
Page 11

(b)

(a)
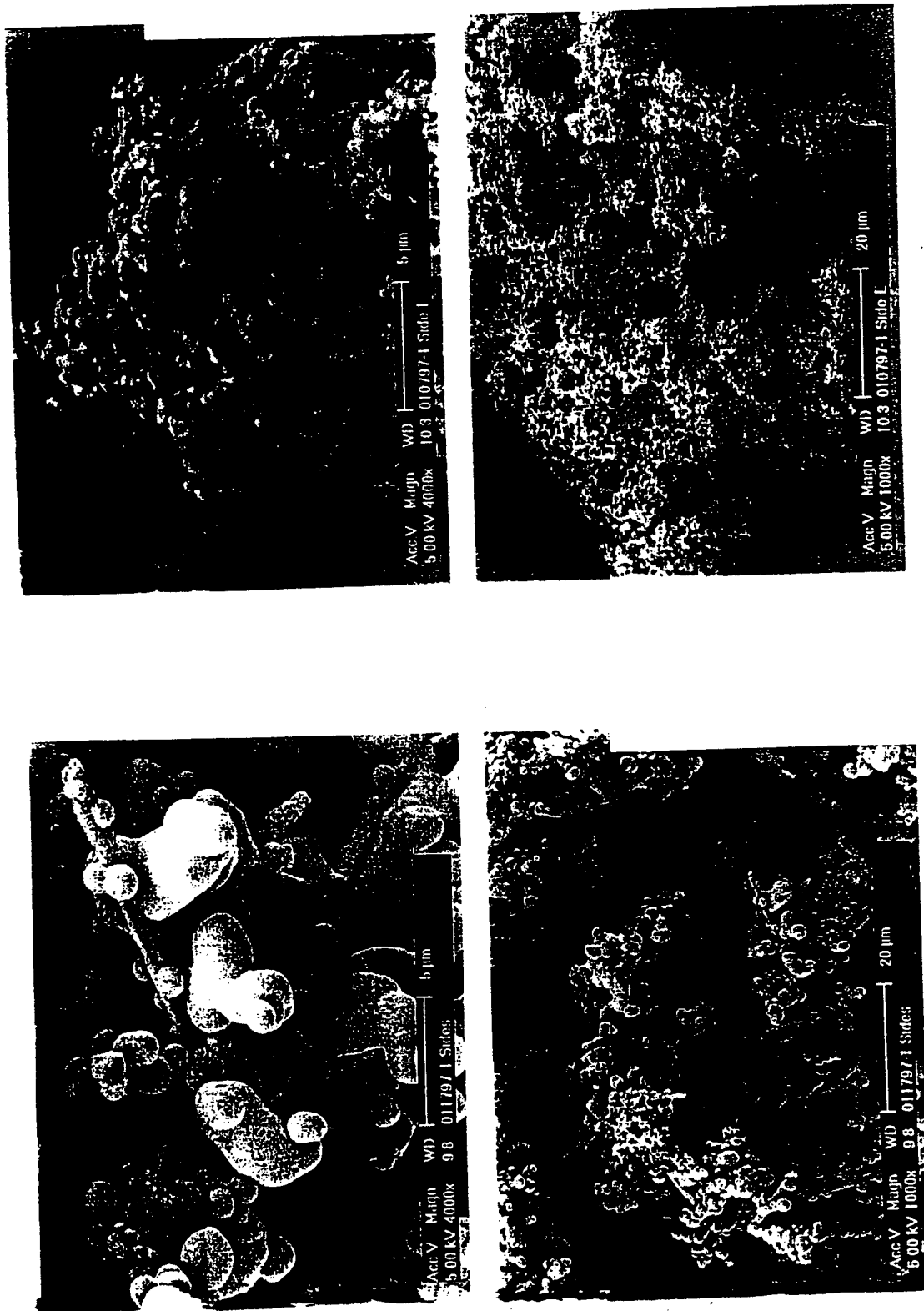
Figure 4.9. Solvent effects on GAS processing results: (a) acetone; (b) MEK.
GAS processing conditions: 2.5% epoxy; 900 psi; 180 μm nozzle; co-current flow; 5 ml/min - 5 min; 0.02 wt% Pluronic.
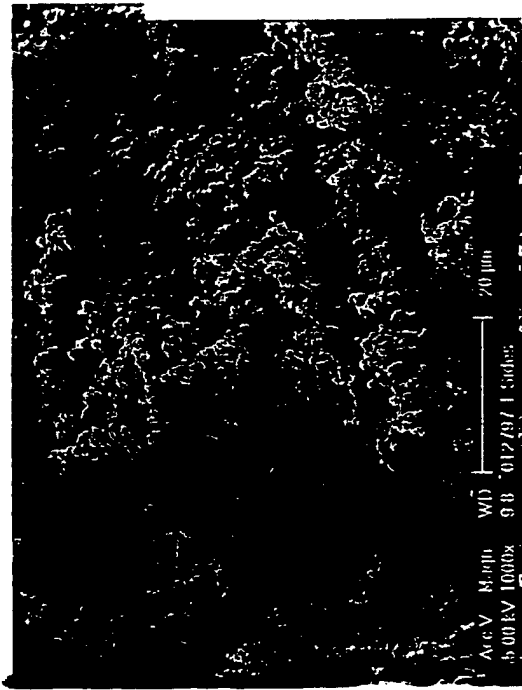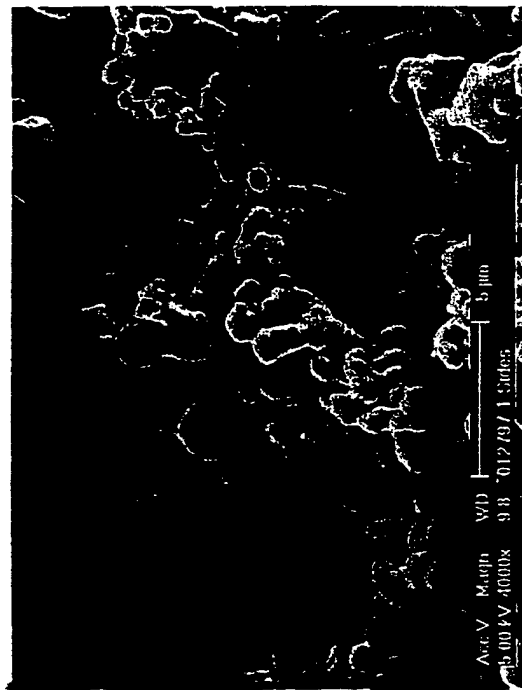
(a)
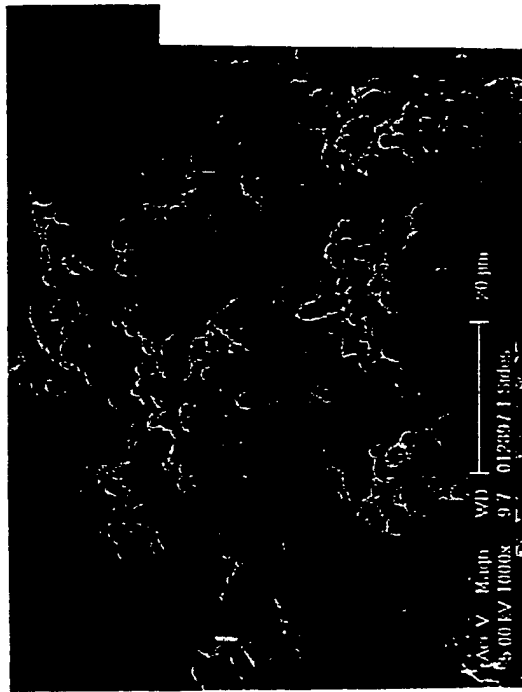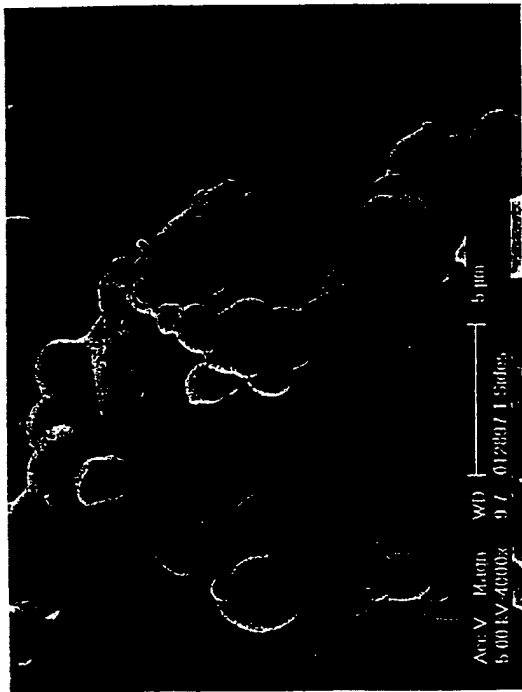
(b)

Figure 4.10. GAS processing of high concentration polymer solution in MEK:
(a) 10 wt% epoxy solution at 1400 psi; (b) 25 wt% epoxy solution at 900 psi.
GAS processing conditions: 180 μm nozzle; counter flow; 0.5 ml/min - 25 min; 0.03 wt% Pluronic.

(b)

(a)
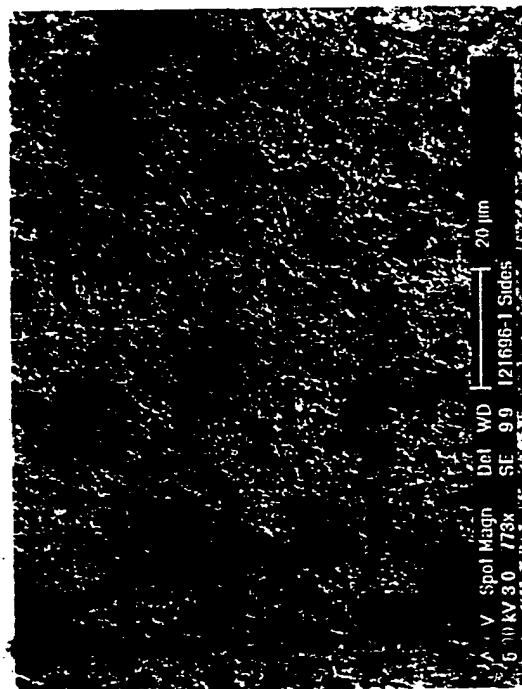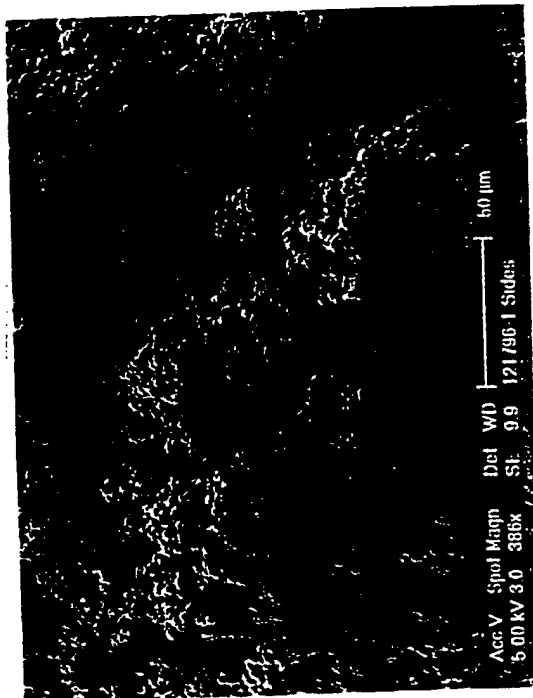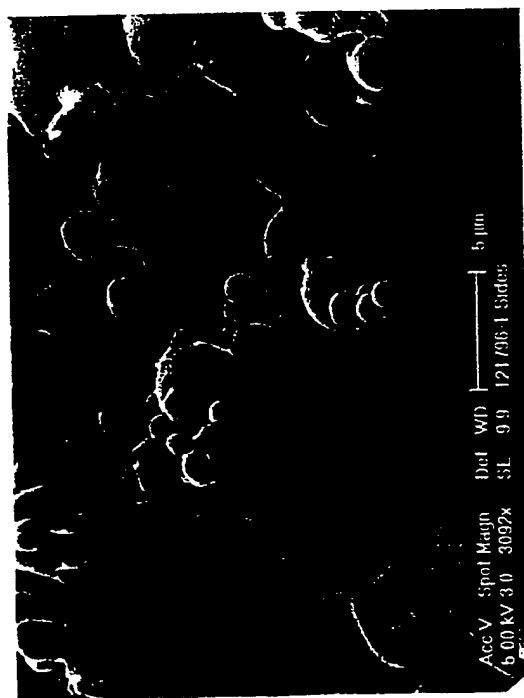
Figure 4.11. Effects of CO_2 flow direction GAS processing results for MEK: (a) co-current flow; (b) counter-current flow. GAS processing conditions: 10% epoxy in MEK; 900 psi; 760 μm nozzle; co-current flow; 0.5 ml/min - 25 min; no surfactant.
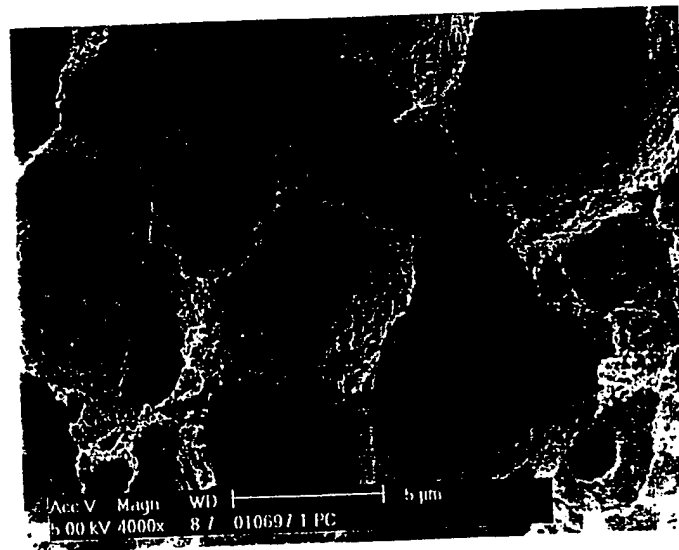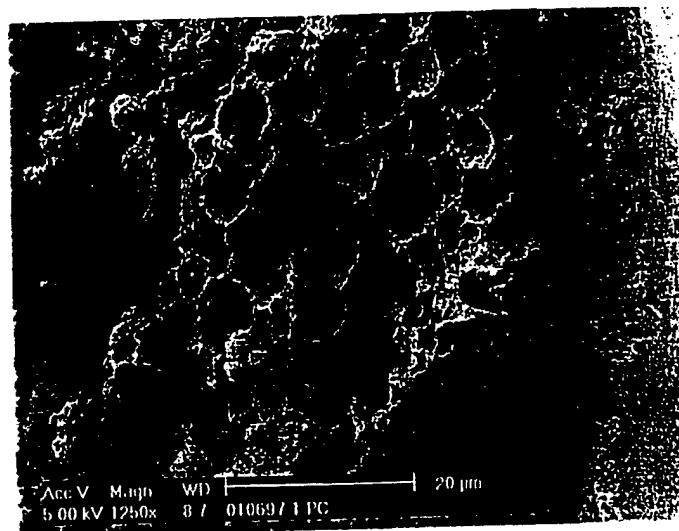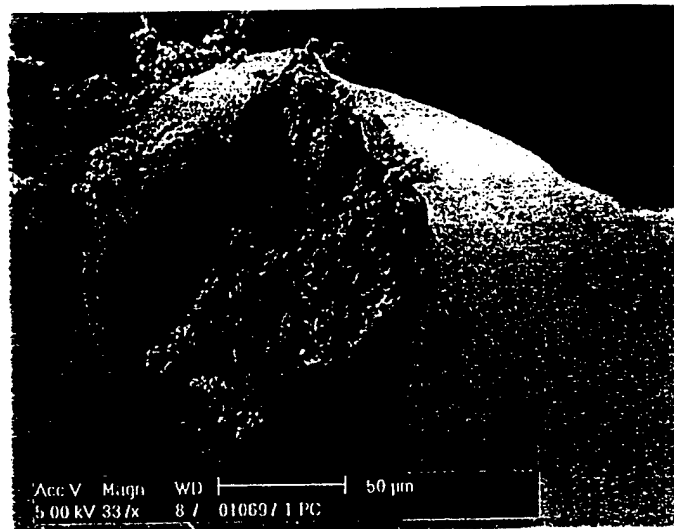
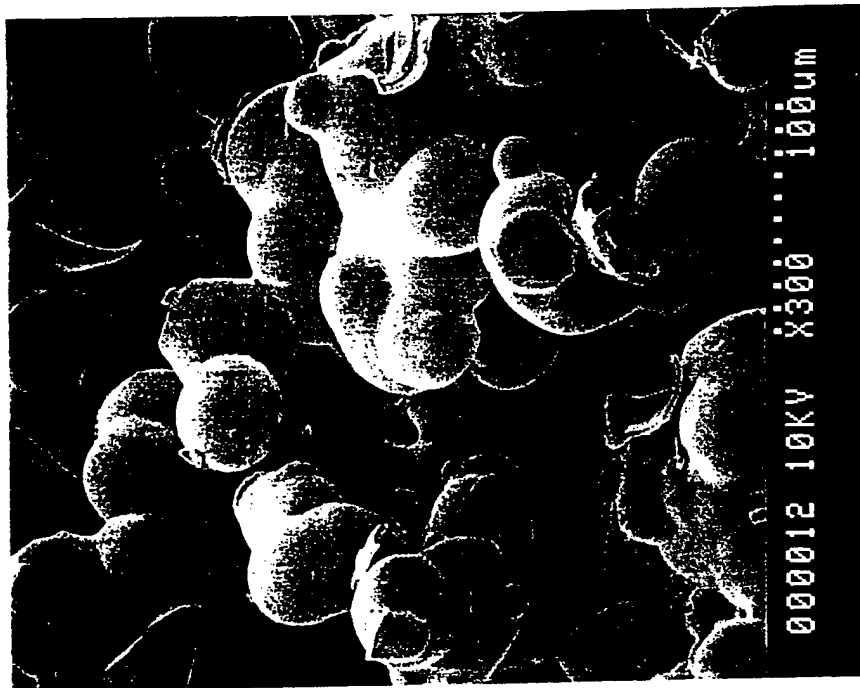**Figure 4.12.** Vesiculated polymer morphology created by GAS processing.

Figure 4.14. Polymer beads created by inkjet processing a 10 wt% solution of epoxy in acetone.

Figure 4.13. Polymer beads created by inkjet processing a 5 wt% solution of epoxy in acetone.

Figure 4.16. Polymer beads created by inkjet processing a 25 wt% solution of epoxy in acetone.
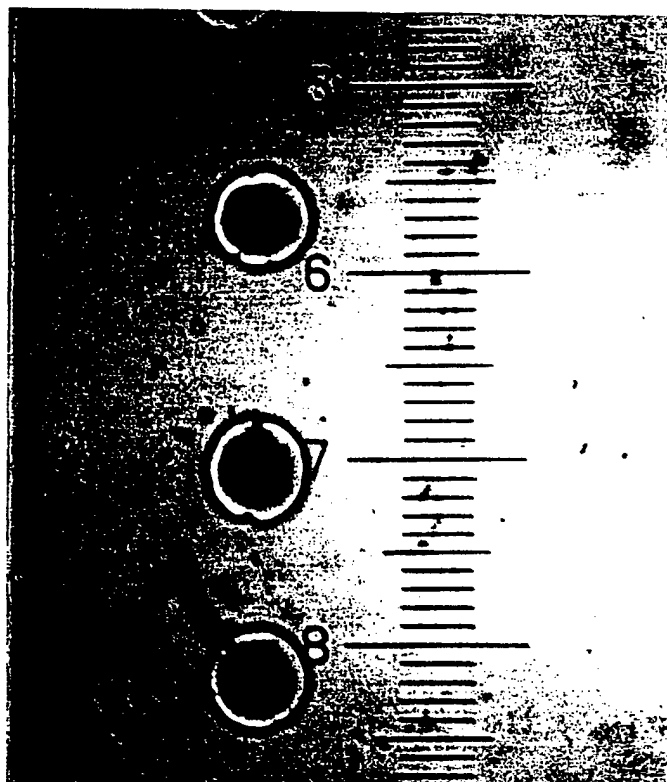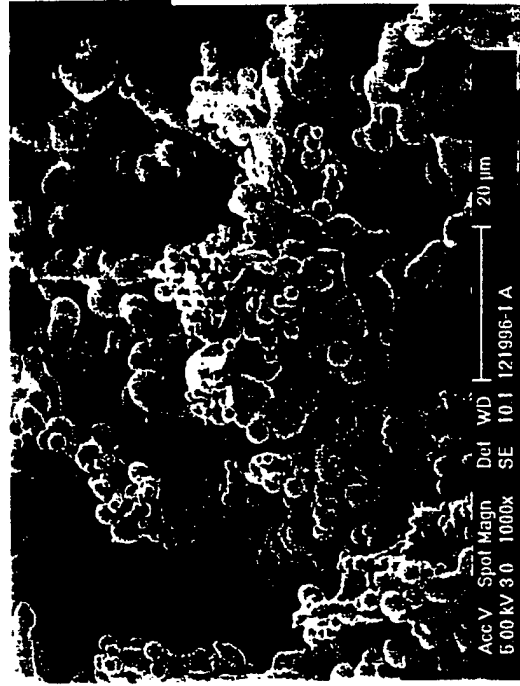

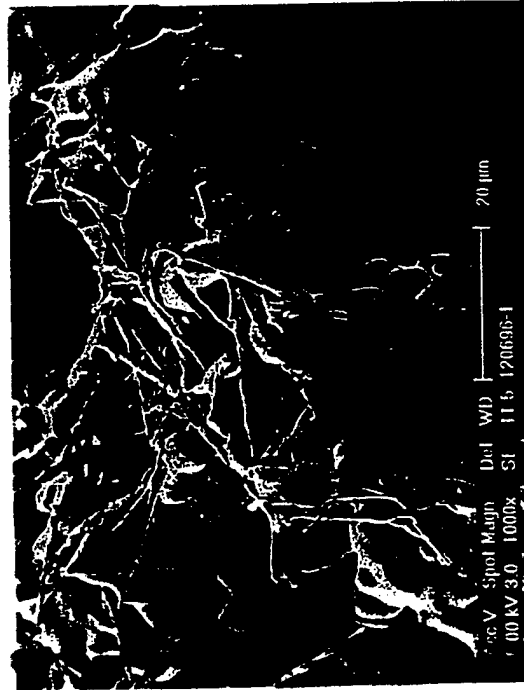**Figure 4.15.** Polymer beads created by inkjet processing a 20 wt% solution of epoxy in acetone.
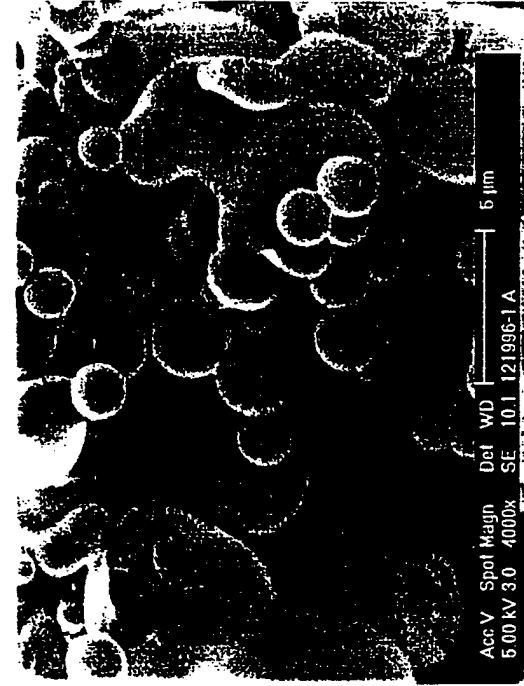
Figure 4.17. Mono-disperse polymer beads created by acoustic printing methods. Droplets were collected on glass slide during production. Actual droplet diameter is approximately 120 μm. Scale is 50 μm per division.

(a)

(b)

Figure 5.1. Evolution of GAS processing results under current program from (a) start to (b) finish.